Retention of fission product caesium in ZrC-coated fuel particles for high-temperature gas-cooled reactors

Kazuo Minato [a,*], Toru Ogawa [a], Toshio Koya [b], Hajime Sekino [b], Takeshi Tomita [b]

[a] *Department of Materials Science, Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki-ken 319-1195, Japan*
[b] *Department of Hot Laboratories, Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki-ken 319-1195, Japan*

Abstract

The ZrC coating layer is a candidate to replace the SiC coating layer of the Triso-coated fuel particle for high-temperature gas-cooled reactors. To understand mechanisms of the good retention capabilities for fission product caesium of the ZrC Triso-coated fuel particles, the particles after post-irradiation heating tests were examined individually with X-ray microradiography and the caesium inventories of the fuel kernel and coating layers of each particle were measured with gamma-ray spectrometry. The fractional content of ^{137}Cs in the fuel kernel was found to be different from particle to particle though ^{137}Cs was not released from the particles practically. The particles, which showed relatively good retention of ^{137}Cs in the fuel kernels, had radially broken inner pyrolytic carbon layers and deformed fuel kernels. The ZrC layer developed the caesium retention capabilities of the fuel kernel through interaction of ZrC with the fuel kernel. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

In current designs of the high-temperature gas-cooled reactor (HTGR), the Triso-coated fuel particles are used [1–4]. The Triso-coated fuel particle consists of a microspherical fuel and coating layers of porous pyrolytic carbon (PyC), inner dense PyC (IPyC), silicon carbide (SiC), and outer dense PyC (OPyC). The function of these coating layers is to retain fission products within the particle. The porous PyC coating layer, called the buffer layer, attenuates fission recoils and provides void volume for gaseous fission products and carbon monoxide. The IPyC coating layer acts as a containment to gases. The SiC coating layer provides mechanical

strength for the particle and acts as a barrier to the diffusion of metallic fission products which diffuse easily through the IPyC layer. The OPyC coating layer protects the SiC coating layer mechanically.

Although SiC has excellent properties, it gradually loses mechanical integrity at very high temperatures, especially above 1700°C, by thermal dissociation [5–7]. The SiC coating layer is also attacked chemically by fission product palladium whose yield from ^{239}Pu is about tenfold that from ^{235}U [8]. In both the cases, degradation of the SiC coating layer leads to extensive release of fission products from the Triso-coated fuel particle.

To develop the competitive power of HTGR, increases in power density and efficiency are inevitable. The direct helium cycle is an attractive option, where higher performance of fission product retention of the coated fuel particles at high temperatures is required. The favorable performance of plutonium burning and the achievability of very high burnup are advantages of HTGR, where higher resistance of the coating layers to

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[*] Corresponding author. Tel.: +81-29 282 5402; fax: +81-29 282 6442.

E-mail address: minato@popsvr.tokai.jaeri.go.jp (K. Minato).

the chemical attack by fission product palladium is needed.

Zirconium carbide (ZrC) is known as a refractory and chemically stable compound, having a melting point of 3540°C, and melts eutectically with carbon at 2850°C [9]. The ZrC coating layer is a candidate to replace the SiC coating layer of the Triso-coated fuel particle; the resulting particle is termed as ZrC Triso-coated fuel particle.

The results of previous irradiation experiments of the ZrC-coated fuel particles were encouraging [9–12]. It has been demonstrated that the ZrC Triso-coated fuel particle maintains thermochemical stability up to a higher temperature than the normal Triso-coated fuel particle [9,12,13]. In addition, the ZrC coating layer has higher resistance to the chemical attack by fission product palladium than the SiC coating layer [14,15]. To clarify the retention of fission products by the ZrC coating layer, post-irradiation heating tests were performed previously [16,17]. The tests revealed that the ZrC coating layer had much better retention capability for caesium, one of the most important fission products, than the SiC coating layer.

In the present work, the caesium retention capability of the ZrC Triso-coated fuel particles was further studied to clarify mechanisms of the caesium retention. The caesium inventories of the individual particles after the post-irradiation heating tests were measured with gamma-ray spectrometry, while mechanical integrity of the coating layers and migration of heavy metals inside the individual particles were examined with X-ray microradiography.

2. Experimental

2.1. Samples

The samples for the present experiments were three kinds of irradiated ZrC Triso-coated UO_2 particles: as-irradiated particles, particles after post-irradiation heating test at 1600°C for 4500 h [16] and those at 1800°C for 3000 h [17]. The diameter and density of the fuel kernels, as well as the thickness and density of each coating layer are listed in Table 1 [12]. The ZrC coating layer was chemically vapor-deposited by the bromide process [18]. The ZrC Triso-coated fuel particles were irradiated in the form of an annular fuel compact loaded in a gas-swept capsule in the Japan materials testing reactor (JMTR) and then some of them were heated as unbonded particles after electrolytic deconsolidation of the fuel compact. The irradiation temperature was about 900°C and the burnup was 1.5% FIMA [12].

The post-irradiation heating tests were performed with a furnace installed in a hot cell [16,17]. In each test one hundred of the unbonded particles were used.

Table 1
Characteristics of ZrC Triso-coated fuel particles

	Diameter or thickness (µm)	Density (mg/m^3)
UO_2 kernel	608 ± 21[a]	10.6
Buffer layer	64 ± 9[a]	1.11
IPyC layer	26 ± 3[a]	1.84
ZrC layer	31[b]	6.6
OPyC layer	55[b]	1.95

[a] (mean) ± (S.D.).
[b] No statistical data were available.

During the heating test, fission gas release was monitored with an ionization chamber and metallic fission products released from the particles were measured with gamma-ray spectrometry of the graphite components of the furnace. No rapid release of fission gas was observed, meaning that no through-coating failure occurred. However, ruthenium, caesium and europium were observed to be released from the particles. The fission product released significantly was ^{106}Ru, whose fractional release was 0.13 at 1600°C for 4500 h and 0.86 at 1800°C for 3000 h. Caesium was retained fairly well, where the fractional release of ^{137}Cs was much less than 10^{-3} in each test. The fractional release of ^{154}Eu was less than 10^{-2} in each test. The results of the heating tests have been reported elsewhere [16,17].

2.2. Procedure

Fifteen ZrC Triso-coated fuel particles were randomly sampled after the two post-irradiation heating tests. Fifteen as-irradiated particles were also sampled for comparison. The individual ZrC Triso-coated fuel particles were named for convenience in a study of the behavior of the individual particles. Once uniquely identified, the individual particle identities were maintained throughout the present experiment.

The individual particles were examined with X-ray microradiography, and fission product inventories of the individual particles were measured with gamma-ray spectrometry. For a study of the fission product behavior in coated fuel particles, each particle was crushed with a specially designed apparatus to recover the fuel kernel and the coating layers separately, and fission product inventories of the fuel kernel and coating layers of each particle were then measured with gamma-ray spectrometry.

Ceramographic observation was made of the coated fuel particles other than those for X-ray microradiography and gamma-ray spectrometry. Since it is impossible to observe the behavior of the whole particle with ceramography after crushing the particle for gamma-ray spectrometry, newly sampled particles were used for ceramography. The particles were examined with X-ray

microradiography, and then embedded in epoxy resin and polished with the standard hot-cell ceramography technique.

3. Results

3.1. Gamma-ray spectrometry

Fig. 1 shows stereomicrographs of a ZrC Triso-coated fuel particle before crushing, and a recovered fuel kernel and fragmented coating layers after crushing, as typical examples. The kernels were recovered as spheres, and almost all the fragments of the coating layers were collected. In the gamma-ray spectrometry, ^{137}Cs ($t_{1/2} = 30.07$ yr), ^{134}Cs ($t_{1/2} = 2.062$ yr), ^{106}Ru ($t_{1/2} = 373.59$ d), ^{144}Ce ($t_{1/2} = 284.893$ d) and ^{154}Eu ($t_{1/2} = 8.593$ yr) [19] were detected but only the amount of ^{137}Cs was measured quantitatively. The inventory of ^{137}Cs

measured on the whole particle before crushing was in good agreement with the sum of the inventories measured on the fuel kernel and the coating layers for each particle.

To compare the behavior of fission product retention among individual particles, the activity ratio ^{137}Cs/^{144}Ce is usually used to account for variations in kernel size and to minimize the effect of small differences in burnup among the particles [20], since cerium forms chemically stable compounds in oxide fuels which tend to remain in the fuel kernel even at very high temperatures. In the present experiment, however, the inventory of ^{137}Cs was divided by the volume of the fuel kernel for each particle and normalized to the mean value, since the amount of ^{144}Ce could not be treated quantitatively. The volume of the fuel kernel for each particle was calculated on the basis of the measured diameter of the individual fuel kernel with the X-ray microradiography.
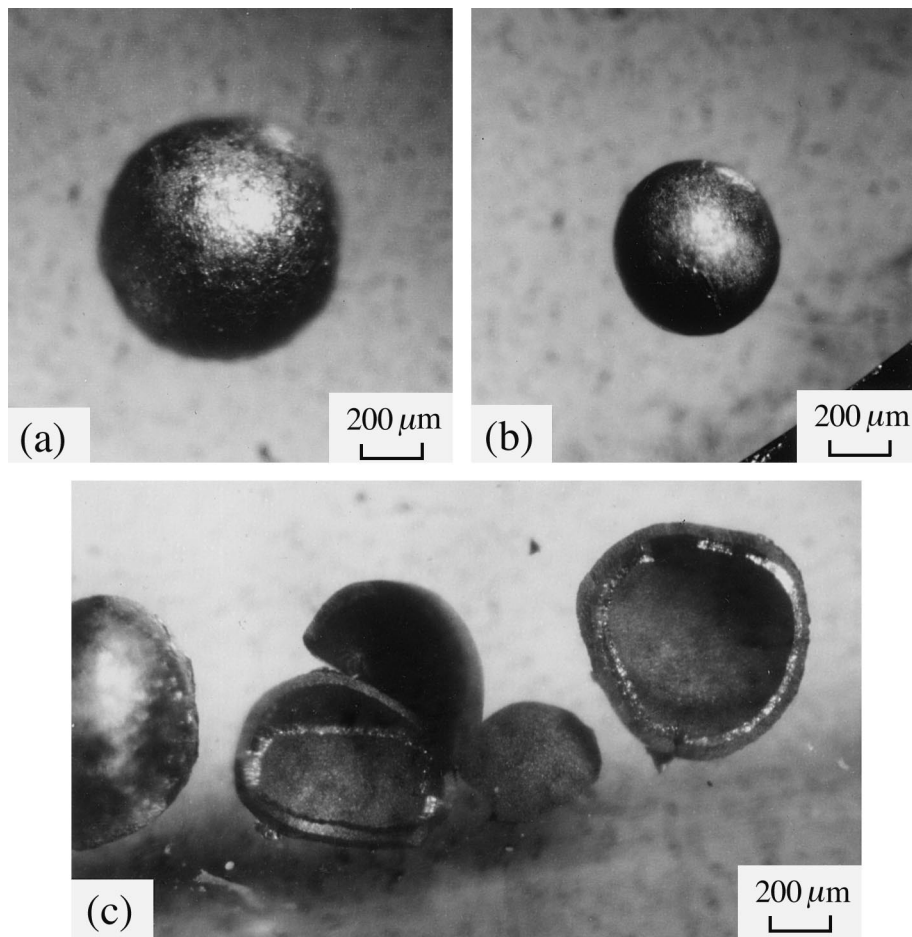

Fig. 1. Stereomicrographs of the ZrC Triso-coated fuel particle before and after crushing: (a) particle before crushing; (b) recovered fuel kernel and (c) fragmented coating layers.

3.1.1. As-irradiated particles

For the as-irradiated coated fuel particles, the normalized ^{137}Cs inventories of the individual particles agreed with each other with the standard deviation of 3.9%, meaning that the irradiation performance of each particle was similar to each other. Fig. 2 shows the fractional contents of ^{137}Cs in the fuel kernel and the coating layers for each as-irradiated particle in order of the fractional content in the fuel kernel. In all the particles, about 98% of ^{137}Cs was retained in each kernel, or about 2% of ^{137}Cs was released from each kernel to the coating layers. The ^{137}Cs retention behavior of each particle during the irradiation was similar to each other.

The release of ^{137}Cs from the fuel kernel could be attributed to the fission recoil. The fractional release from the kernel by the fission recoil, F_r, is expressed by

$$F_r = (3/4)(r/a) - (1/16)(r/a)^3, \qquad (1)$$

where a is the radius of the kernel and r is the recoil range [21]. When a is 304 μm and r is 8 μm [22], the fractional release by the fission recoil is obtained to be 0.02. This value agreed quite well with that obtained by the gamma-ray spectrometry. The release by diffusion could be negligible since the irradiation temperature was about 900°C.

3.1.2. Particles after heating tests

The gamma-ray spectrometry on the whole particles after the heating test at 1600°C for 4500 h revealed that there was only a small variation in the normalized ^{137}Cs inventories with the standard deviation of 3.4% and the mean value agreed quite well with that for the as-irradiated particles. This result indicated that ^{137}Cs was retained very well in all the particles during the heating test, which was consistent with the result of the metallic fission product release measurement that the fractional

release of ^{137}Cs was 3.0×10^{-4} at the end of the heating test [16].

Fig. 3 shows the fractional contents of ^{137}Cs in the fuel kernel and the coating layers for each particle after the heating test at 1600°C for 4500 h in order of the fractional content in the kernel. It was found that the fractional content of ^{137}Cs in the kernel was smaller than that of the as-irradiated particles and was not constant but varied largely from particle to particle. The fractional content in the kernel ranged from 0.05 to 0.93. It should be noted that the first four particles showed good retention of ^{137}Cs by the fuel kernel. Although ^{137}Cs was not released from the particles practically, the distributions of ^{137}Cs in the particles were found to be different from particle to particle.

The gamma-ray spectrometry on the particles after the heating test at 1800°C for 3000 h showed the same tendency as described above. The normalized ^{137}Cs inventories in the whole particle agreed with each other with the standard deviation of 3.9% and the mean value agreed well with that for the as-irradiated particles. In all the particles ^{137}Cs was retained very well during the heating test, which was consistent with the fractional release of ^{137}Cs of 4.2×10^{-4} measured in the heating test [17].

Fig. 4 shows the fractional contents of ^{137}Cs in the fuel kernel and the coating layers for each particle. It was found again that the part of ^{137}Cs was released from the kernel to the coating layers in each particle during the heating test and that the fractional content of ^{137}Cs in the kernel was different from particle to particle though ^{137}Cs was not released from the particles practically. The fractional content of ^{137}Cs in the kernel ranged from 0.03 to 0.63. It could be seen in Fig. 4 that the fifteen particles were divided into two groups in terms of the fractional content of ^{137}Cs in the fuel kernel. The first seven particles retained ^{137}Cs in the fuel kernels

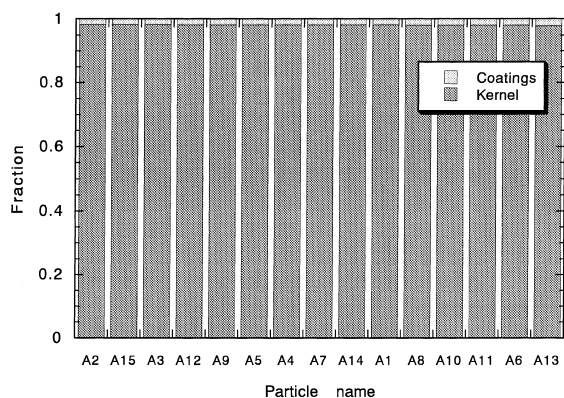
Fig. 2. Fractional contents of ^{137}Cs in the fuel kernel and coating layers for each as-irradiated ZrC Triso-coated fuel particle.
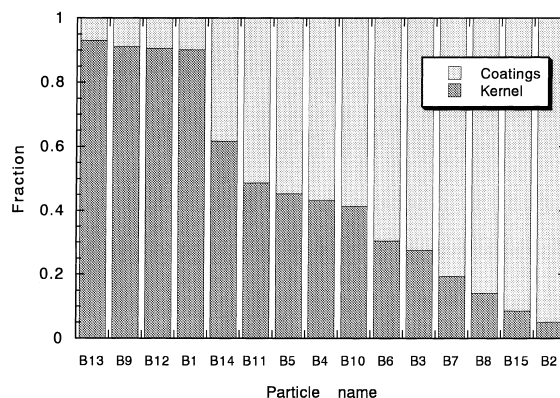

Fig. 3. Fractional contents of ^{137}Cs in the fuel kernel and coating layers for each ZrC Triso-coated fuel particle after post-irradiation heating test at 1600°C for 4500 h.
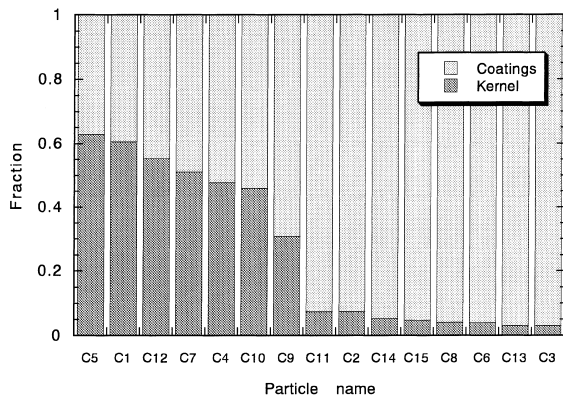
Fig. 4. Fractional contents of ^{137}Cs in the fuel kernel and coating layers for each ZrC Triso-coated fuel particle after post-irradiation heating test at 1800°C for 3000 h.

relatively well, whereas the other eight particles showed poor ^{137}Cs retention in the fuel kernels.

3.2. X-ray microradiography

The as-irradiated particles and the particles after the heating tests were examined individually with the X-ray microradiography before crushing the particles. No anomaly was found on all the as-irradiated particles, whereas changes were observed on some of the particles after the heating tests. Fig. 5 shows typical examples of X-ray microradiographs taken from the particles after the heating test at 1800°C for 3000 h. Anomaly was neither found on eleven out of the fifteen particles after the heating test at 1600°C for 4500 h, nor on eight out of the fifteen particles after the heating test at 1800°C for 3000 h. The rest of the particles showed changes like Fig. 5(b) and (c), which must have occurred during the heating tests.

Fig. 5(b) shows the particle with the buffer and IPyC layers broken radially and the fuel kernel deformed there. A ceramograph of the particle of this kind is shown in Fig. 6 and a stereomicrograph of the fuel kernel of this kind is shown in Fig. 7. The deformation of the fuel kernel is seen like mountain ranges in Fig. 7. In the particles of this kind, the ZrC coating layers and fuel kernels interacted through the gas phase [23]. The X-ray microradiograph in Fig. 5(c) shows the particle whose fuel kernel was abnormal at the periphery, though no failure of the IPyC coating layer was observed with the X-ray microradiography. Actually, the deformation of the fuel kernel like Fig. 7 was always observed by the stereomicrography after crushing the particles of this kind. This probably means that the particles like Fig. 5(c) had radially broken IPyC coating layers with the deformed fuel kernels, which could not
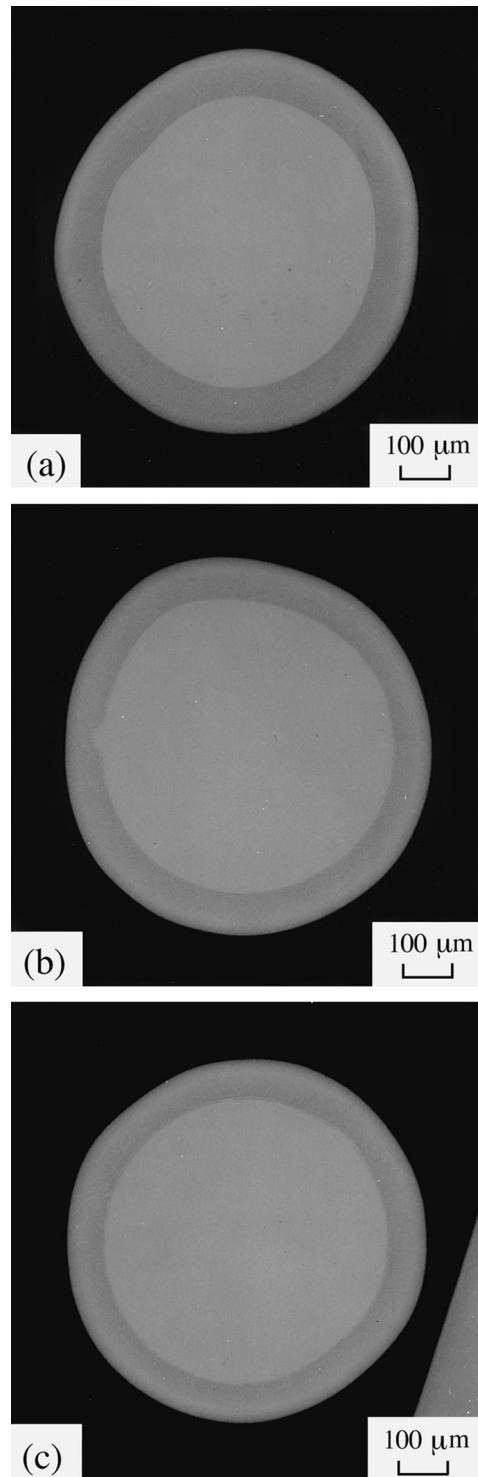

Fig. 5. X-ray microradiographs of the ZrC Triso-coated fuel particles after post-irradiation heating test at 1800°C for 3000 h: (a) without anomaly (C11); (b) with buffer and IPyC layers broken radially and fuel kernel deformed there (C12) and (c) with periphery of fuel kernel abnormal (C1).
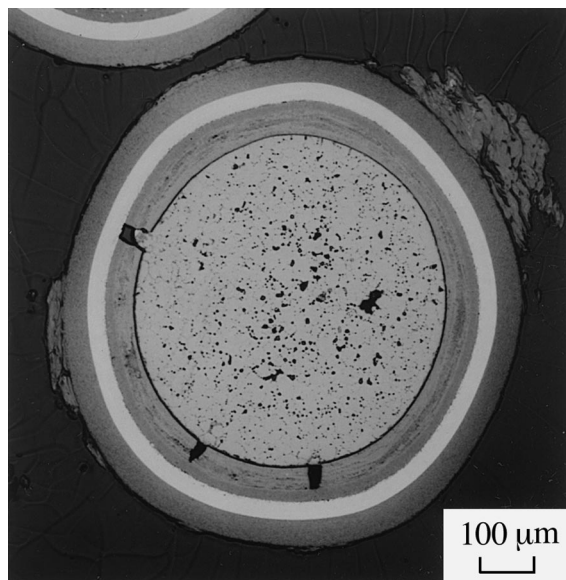
Fig. 6. Ceramograph of the ZrC Triso-coated fuel particle with buffer and IPyC layers broken radially and fuel kernel deformed there after post-irradiation heating test at 1800°C for 3000 h.

be observed with the X-ray microradiography performed from only one direction.

4. Discussion

When the result of the X-ray microradiography was combined with that of the gamma-ray spectrometry, a
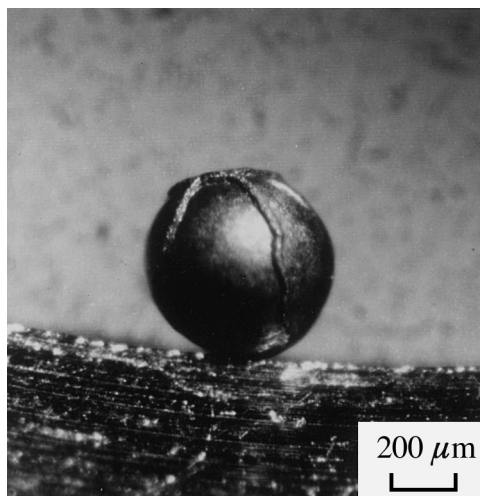

Fig. 7. Stereomicrograph of the deformed fuel kernel of the ZrC Triso-coated fuel particle after post-irradiation heating test at 1800°C for 3000 h.

surprising relation was found between them. The relation was that the first four particles in Fig. 3 and the first seven particles in Fig. 4, which showed relatively good retention of ^{137}Cs in the fuel kernels, were found to have radially broken IPyC layers and deformed fuel kernels. The rest of the particles after the heating tests, whose caesium retention capabilities of the fuel kernels were relatively poor, showed no anomaly in the X-ray microradiography. This relation indicated two aspects of the ZrC layer. One is that the ZrC layer had good retention capabilities for caesium as a barrier. The other is that the ZrC layer developed the caesium retention ca-
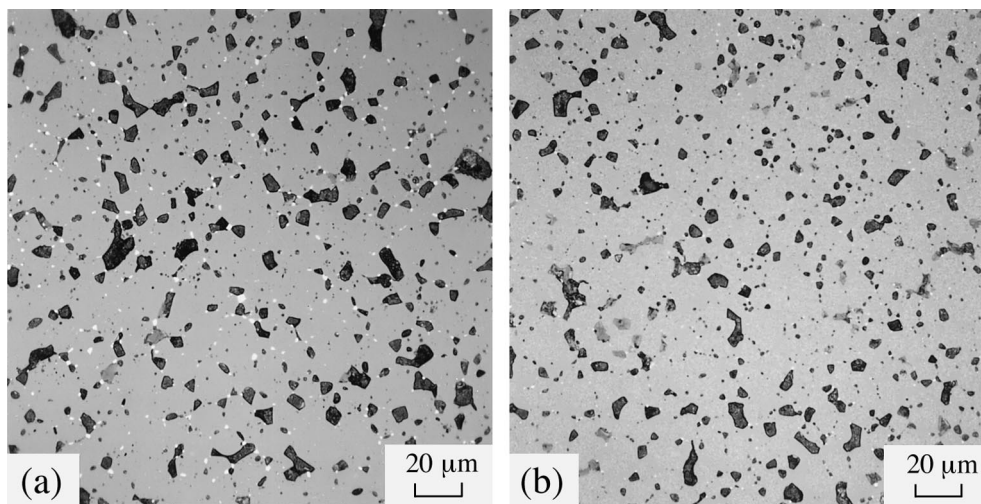

Fig. 8. Ceramographs of the fuel kernels of the ZrC Triso-coated fuel particles after post-irradiation heating test at 1800°C for 3000 h (a) without anomaly and (b) with buffer and IPyC layers broken radially and fuel kernel deformed there.

pabilities of the fuel kernel through interaction of ZrC with the fuel kernel.

When the IPyC coating layer fails, the ZrC coating layer comes into touch with CO gas which is produced by the reaction of the buffer layer with the liberated oxygen from UO_2 during fission. The thermodynamic analysis showed that ZrC would react with CO to form ZrO_2 and C under relevant conditions [23]. This reaction results in reduction of the oxygen potential of the fuel, which may influence chemical forms of the fission products in the fuel. In this case, ZrC functions as an oxygen getter. Bullock and Kaae [24] have reported on the coated UO_2 particles gettered with ZrC, where ZrC was coated on the UO_2 kernel or ZrC was dispersed throughout the buffer layer. In these particles ZrC was intended to be used as an oxygen getter.

Fig. 8 shows ceramographs of the fuel kernels with and without anomaly observed with the X-ray microradiography. The appearances are somewhat different from each other. Many metallic inclusions are seen in the fuel kernel without anomaly by the X-ray microradiography, whereas the metallic inclusions are inconspicuous in the deformed fuel kernel. As the oxygen potentials of the fuels were considered to be different from each other, the chemical forms of the fission products must have been influenced.

The thermodynamic analysis of the chemical forms of the fission products in the fuel was tried to clarify the mechanisms of the development of caesium retention capabilities of the fuel kernel through interaction of ZrC with the fuel kernel. The method of the thermodynamic analysis was the same as used in the previous analysis [25]. As caesium containing species, Cs_2ZrO_3, Cs_2MoO_4, Cs_2UO_4, CsI, etc., and intercalation compounds with carbon were considered in the analysis, but the development of the caesium retention capabilities of the fuel kernel could not be related to the addition of ZrC as a getter.

Although the mechanisms of the development of caesium retention capabilities of the fuel kernel are not understood well, an additional ZrC coating layer on the UO_2 kernel of the ZrC Triso-coated fuel particle would enhance the caesium retention capabilities.

5. Conclusions

To understand the mechanisms of the good retention capabilities for fission product caesium of the ZrC Triso-coated fuel particles, the particles after post-irradiation heating tests were examined individually with X-ray microradiography, while the caesium inventories of the fuel kernel and coating layers of each particle were measured with gamma-ray spectrometry. The following were concluded:

1. Part of ^{137}Cs was released from the kernel to the coating layers in each particle during the heating tests and the fractional content of ^{137}Cs in the kernel was different from particle to particle though ^{137}Cs was not released from the particles practically.
2. The ZrC Triso-coated fuel particles, which showed relatively good retention of ^{137}Cs in the fuel kernels, had radially broken IPyC layers and deformed fuel kernels. The particles whose caesium retention capabilities of the fuel kernels were relatively poor showed no anomalies in the X-ray microradiography.
3. The ZrC layer developed the caesium retention capabilities of the fuel kernel through interaction of ZrC with the fuel kernel though the mechanisms could not be understood well. An additional ZrC coating layer on the UO_2 kernel of the ZrC Triso-coated fuel particle would enhance the caesium retention capabilities.

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