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Journal of Nuclear Materials 252 (1998) 13–21

journal of nuclear materials

Deterioration of ZrC-coated fuel particle caused by failure of pyrolytic carbon layer

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Received 18 July 1997; accepted 12 October 1997

Abstract

The ZrC coating layer is a candidate to replace the SiC coating layer of the Triso-coated fuel particles for high-temperature gas-cooled reactors. To understand the behavior of the ZrC–Triso-coated fuel particles at 1800 to 2000°C, a ceramographic examination and an electron probe microanalysis were performed on the ZrC–Triso-coated fuel particles after the post-irradiation heating tests and a thermodynamic analysis of the Zr–C–U–O system was carried out. Based on the results of the examination and analyses, a mechanism of the deterioration of the ZrC–Triso-coated fuel particles was proposed. The deterioration of the ZrC–Triso-coated fuel particles observed at 1800 to 2000°C was caused by the failure of the inner pyrolytic carbon layer. © 1998 Elsevier Science B.V.

1. Introduction

The high temperature gas-cooled reactor (HTGR) uses coated fuel particles, which are dispersed in a graphite matrix to form a fuel element. In current HTGR designs the Triso-coated fuel particles are to be used [1–4]. The Triso-coated fuel particle consists of a microspherical kernel of oxide or oxycarbide 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.

Zirconium carbide (ZrC) is known as a refractory compound, having a melting point of 3540°C, and melts eutectically with carbon at 2850°C [5]. The ZrC coating layer is a candidate to replace the SiC coating layer of the Triso-coated fuel particles; the resulting particle is termed ZrC–Triso-coated fuel particle.

The review and evaluation of the ZrC coating layer for HTGR fuel particles have been made by Kasten et al. [6] and Minato et al. [7]. The results of irradiation experiments of the ZrC-coated fuel particles were encouraging for their use [5,8–10]. It has been demonstrated that the ZrC–Triso-coated fuel particles have much higher temperature stability than the normal Triso-coated fuel particles [5,10,11]. In addition, the ZrC coating layers have higher resistance to chemical attack by fission product palladium than the SiC coating layers [12,13].

To clarify the retentivity of fission products by the ZrC coating layer, the post-irradiation heating tests at 1600, 1800 and 2000°C were performed previously by the authors [14,15]. The tests showed that the ZrC–Triso-coated fuel particles had much better retentivity for fission gas and one of the most important fission products of cesium than the normal Triso-coated fuel particles. However, in the post-irradiation heating tests at 1800 and 2000°C, deterioration of the ZrC layer was observed, which re-

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PII S0022-3115(97)00319-X

Table 1
Characteristics of ZrC–Triso-coated fuel particles

	Diameter or thickness (μm)	Density (Mg/m^3)
UO_2 kernel	608	10.6
Buffer layer	64	1.11
IPyC layer	26	1.84
ZrC layer	31	6.6
OPyC layer	55	1.95

sulted in the release of a large amount of cesium at 2000°C [15].

In the present work, a ceramographic examination and an electron probe microanalysis were performed on the ZrC–Triso-coated fuel particles after the previous post-irradiation heating tests and a thermodynamic analysis of the Zr–C–U–O system was carried out to study the mechanism of the deterioration of the ZrC–Triso-coated fuel particles at 1800 to 2000°C.

2. Ceramography and electron probe microanalysis

2.1. Experimental

2.1.1. Samples

The samples examined were the ZrC–Triso-coated UO_2 particles after the post-irradiation heating tests [15]. The diameter and density of the fuel kernels and the thickness and density of the coating layers are listed in Table 1. The ZrC–Triso-coated fuel particles were irradiated in the form of a fuel compact in the Japan Materials Testing Reactor (JMTR) and heated as unbonded particles after deconsolidation of the fuel compact. The irradiation and heating conditions of the samples [10,15] are shown in Table 2. The irradiation temperature was about 900°C and the burnup was 1.5% FIMA. The heating tests were performed at 1800°C for 3000 h and at 2000°C for 100 h, respectively.

2.1.2. Methods

The unbonded ZrC–Triso-coated fuel particles were embedded in epoxy resin and polished with the standard hot-cell ceramography technique. The polished cross section of the particles were examined with an optical microscope and a shielded electron probe microanalyzer (EPMA). Gold was vapor deposited on the polished surface to prevent the samples from charging during the analysis.

Table 2
Irradiation and heating conditions of ZrC–Triso-coated fuel particles

	Duration	Temperature (°C)	Burnup
Irradiation	79.9 EFPD	900	1.5% FIMA
Heating-1	3000 h	1800	–
Heating-2	100 h	2000	–

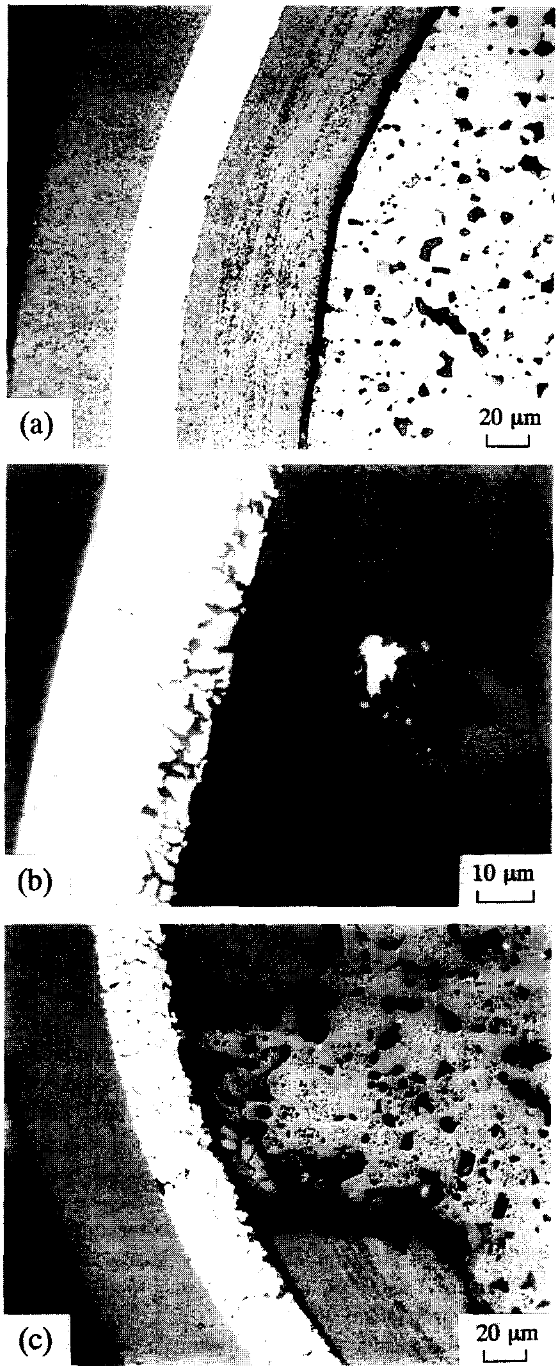

Fig. 1. Optical micrographs of polished cross section of irradiated ZrC–Triso-coated fuel particles; (a) and (b) after heating at 1800°C for 3000 h and (c) after heating at 2000°C for 100 h.

The morphology of the ZrC coating layers was observed with an optical microscope after the ZrC coating layers of the polished surface were etched chemically. The samples were dipped in the etchant of the mixture of HF, HNO_3 and H_2O in the ratio 3:1:1 for a few seconds.

2.2. Results

Fig. 1 shows typical optical micrographs of the deteriorated ZrC–Triso coated fuel particles in the order of deterioration after post-irradiation heating (1800°C for 3000 h or 2000°C for 100 h). Some of the optical micrographs have been shown in the previous paper [15].

After heating at 1800°C for 3000 h, most of the particles had intact coating layers observed by X-ray microradiography [15] and optical micrography. The particle shown in Fig. 1(a), heated at 1800°C for 3000 h, revealed no coating failure though the inner and outer surfaces of the ZrC coating layer were not smooth and some white spots were present in the IPyC coating layer. Fig. 2 shows the secondary electron image and X-ray images of zirconium, carbon and uranium at about the same position as Fig. 1(a). The white spots in the IPyC coating layer were found to consist mainly of zirconium, which probably came from the ZrC coating layer. An unexpected result was that uranium was distributed at the interface between the IPyC and ZrC coating layers and even in the ZrC coating layer.

Fig. 1(b) shows the particle with failed IPyC and buffer layers after heating at 1800°C for 3000 h. In this particle, the UO_2 kernel was deformed, where some compounds other than UO_2 were present and the inner part of the ZrC coating layer seemed to be attacked along the grain boundaries. The electron probe microanalysis revealed that zirconium was present at the tip of the deformed part of the UO_2 kernel, as shown in Fig. 3. Carbon was also present at the deformed part and the grain boundaries of UO_2. Uranium was distributed much deeper in the ZrC coating layer than that shown in Fig. 2(d).

Most of the ZrC–Triso-coated fuel particles after heating at 2000°C for 100 h showed the failure of the IPyC and buffer layers with severely damaged ZrC coating layers. However, no failure of the OPyC coating layer was found.

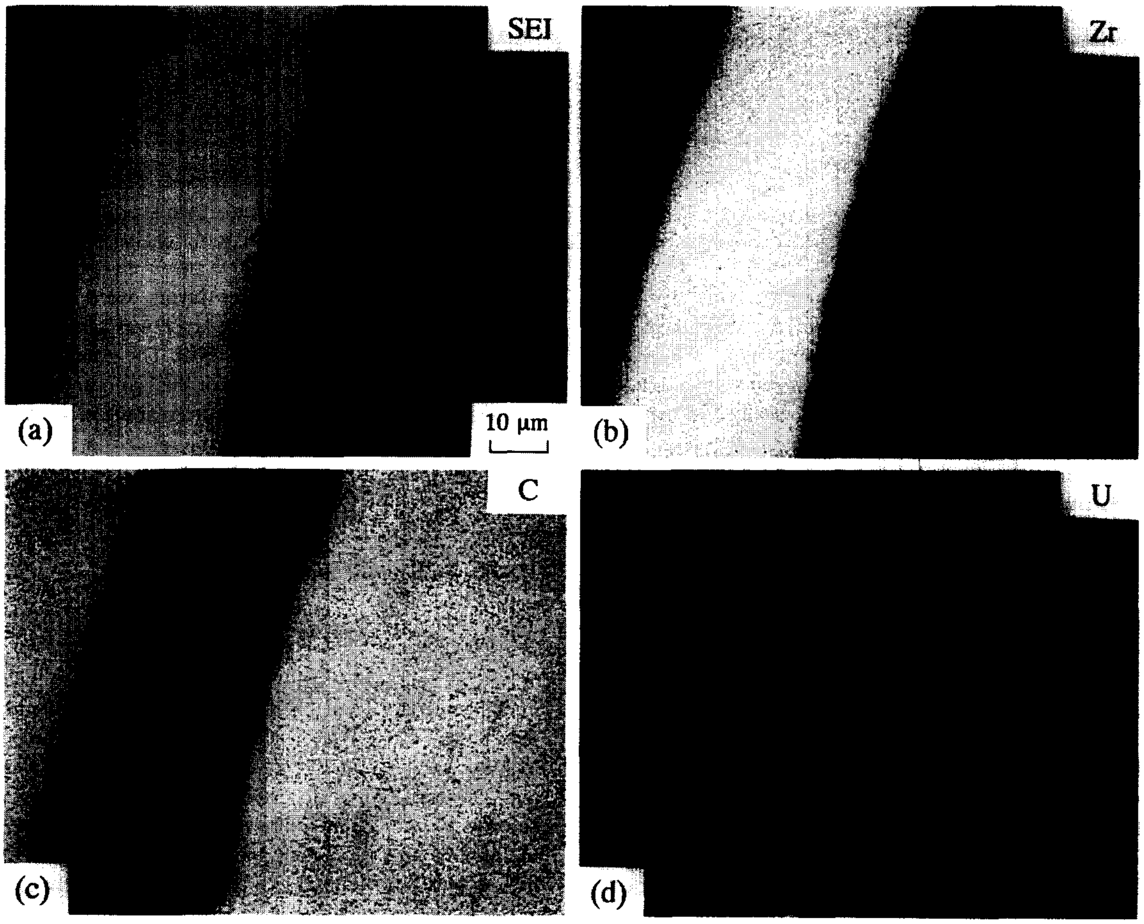

Fig. 2. Electron probe microanalysis of irradiated ZrC–Triso-coated fuel particle after heating at 1800°C for 3000 h shown in Fig. 1(a); (a) secondary electron image, (b) X-ray image for zirconium, (c) X-ray image for carbon and (d) X-ray image for uranium.

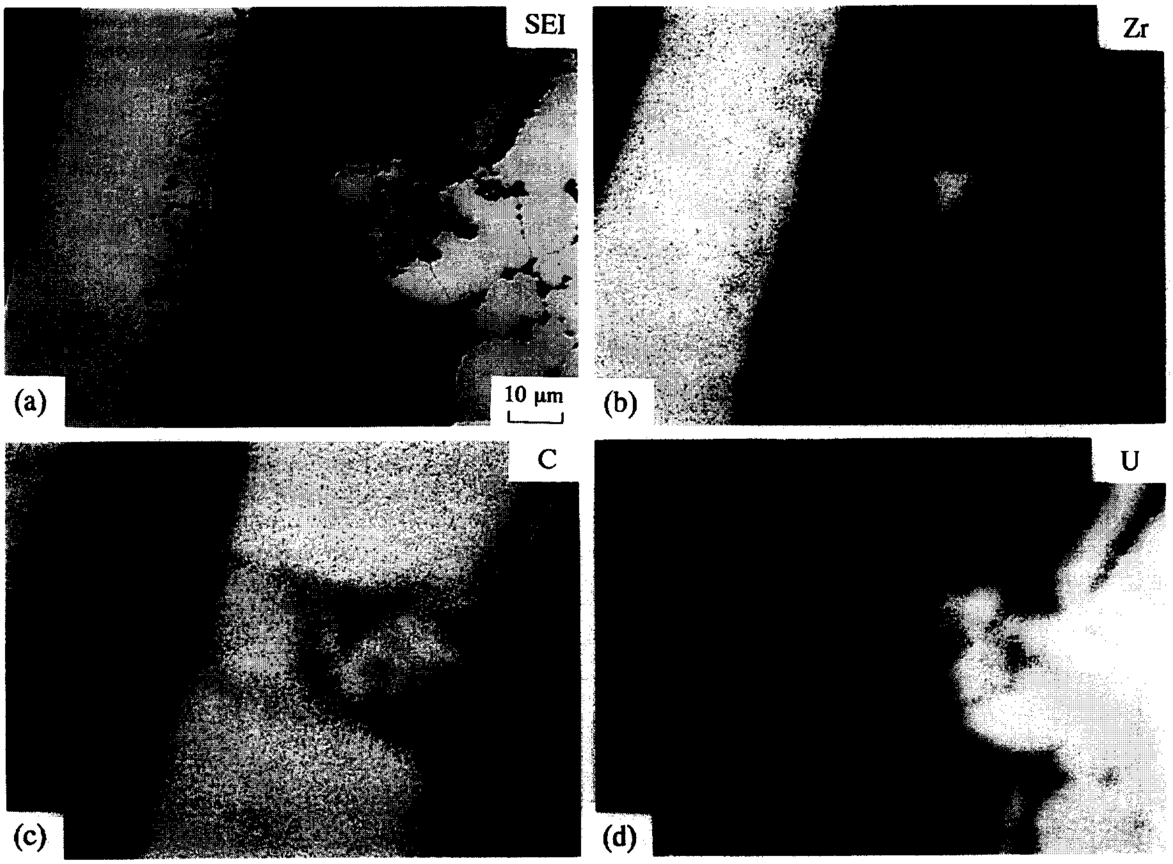

Fig. 3. Electron probe microanalysis of irradiated ZrC–Triso-coated fuel particle after heating at 1800°C for 3000 h shown in Fig. 1(b); (a) secondary electron image, (b) X-ray image for zirconium, (c) X-ray image for carbon and (d) X-ray image for uranium.

The particle shown in Fig. 1(c), heated at 2000°C for 100 h, revealed the failed IPyC and buffer layers and the damaged ZrC coating layer with the deformed fuel kernel. Fig. 4 shows the results of the electron probe microanalysis. It was found that zirconium was distributed in the fuel kernel, which was seen as white spots in Fig. 1(c). Uranium was found to be distributed through the thickness of the ZrC coating layer.

The electron probe microanalysis revealed the presence of zirconium in the fuel kernels and that of uranium in the ZrC coating layers, as shown in Figs. 2–4. However, the chemical states of zirconium and uranium could not be determined.

Fig. 5 shows typical optical micrographs of etched ZrC coating layer after heating at 1800°C for 3000 h. When the IPyC and buffer layers were intact, the grains of the ZrC coating layer were large as shown in Fig. 5(a), which was almost the same morphology as that of an unirradiated ZrC coating layer after heating at 1800°C for 1 h [16]. The ZrC–Triso-coated fuel particles examined in the present study were heat-treated at 1800°C for one hour during the fabrication of the fuel compact. Probably the large grain size did not result from the irradiation and the post-irradiation heating.

When the IPyC and buffer layers were failed, the morphology of the ZrC coating layer was changed from the above case, as shown in Fig. 5(b). The grains were not clearly observed at the inner part of the layer, and the grain size was smaller. This change occurred at the reaction zone of the ZrC coating layer and may be related to the deterioration of the layer.

3. Thermodynamic analysis

3.1. Procedure

To understand the chemical reactions occurred in the deteriorated ZrC–Triso-coated fuel particles, the thermodynamic analysis of the Zr–C–U–O system was carried out. The computer code ChemSage [17] was used, which calculates equilibrium composition and vapor pressure in a multiphase and multicomponent system on the basis of minimization of the total free energy of the system. Chemical species considered in the analysis are listed in Table 3. The thermodynamic data of the chemical species needed for the analysis were taken from the SGTE database [18]

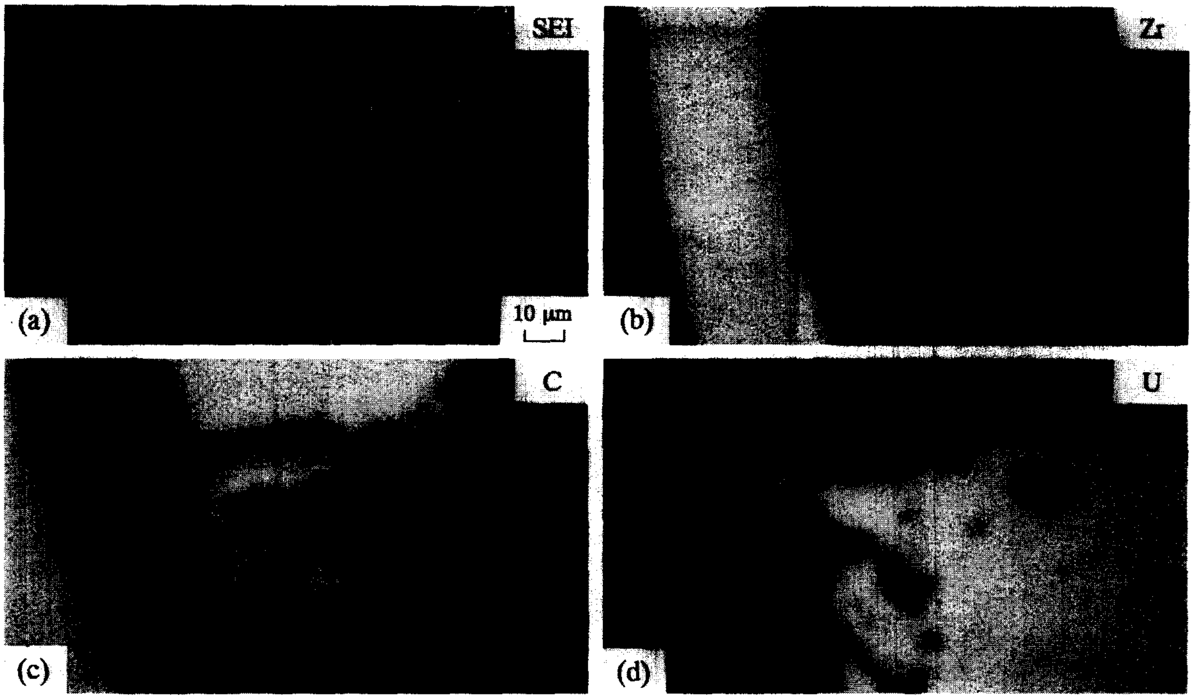

Fig. 4. Electron probe microanalysis of irradiated ZrC–Triso-coated fuel particle after heating at 2000°C for 100 h shown in Fig. 1(c); (a) secondary electron image, (b) X-ray image for zirconium, (c) X-ray image for carbon and (d) X-ray image for uranium.

and the compilation by Cordfunke and Konings [19]. The temperatures were varied from 1200 to 2200°C, and the volume was kept constant. For comparison, a thermodynamic analysis of the Si–C–U–O system was also performed.

3.2. Results

When the IPyC coating layer is failed, the ZrC coating layer is exposed to CO(g) produced by the reaction of the buffer layer with the liberated oxygen from uranium dioxide during fission. Therefore, the reaction of ZrC with CO(g) was analyzed first. Fig. 6 shows the temperature dependence of the equilibrium CO(g) pressure of the reaction, together with that of CO_2(g). From the amounts of the species at equilibrium, the main reaction in the system was found to be expressed by

$$ZrC(s) + 2CO(g) \rightarrow ZrO_2(s) + 3C(s). \qquad (1)$$

In Fig. 6 the temperature dependence of the equilibrium CO(g) and CO_2(g) pressures of the reaction of SiC with CO(g) is also shown for comparison. In this case, the main reaction was expressed by

$$SiC(s) + 2CO(g) \rightarrow SiO_2(s) + 3C(s). \qquad (2)$$

Fig. 6 indicates that the ZrC coating layer would be oxidized to ZrO_2 when exposed to CO(g) of pressures higher than the equilibrium pressure at any temperatures. This sentence is also valid when the words of ZrC and ZrO_2 are replaced by SiC and SiO_2, respectively. The CO(g) pressure in the irradiated Triso-coated UO_2 particles estimated previously [20,21] was higher than the equilibrium CO(g) pressures of the reactions ZrC–CO and SiC–CO, respectively.

In the present thermodynamic analysis, ZrC and ZrO_2 were treated as stoichiometric compounds though this is not strictly true. To check the validity of the assumption, the present result was compared with that of the thermodynamic analysis in which the non-stoichiometry was taken into account [22]. The difference between both the results proved to be small, as shown in Fig. 6. The purpose of the present analysis was attained with the stoichiometric compounds.

Fig. 7 shows the equilibrium partial pressures of the main gaseous species containing zirconium and silicon in the reactions ZrC–CO and SiC–CO, respectively. The main gaseous species were found to be ZrO(g), ZrO_2(g) and Zr(g) in the reaction ZrC–CO, and SiO(g), Si(g) and SiO_2(g) in the reaction SiC–CO. It should be noted that the partial pressure of SiO(g) is much higher than that of ZrO(g) at any temperatures. The high SiO(g) pressure causes the transfer of silicon from the reaction zone of the SiC coating layer, resulting in the deterioration of the SiC coating layer severely [23], when the IPyC coating layer is failed.

Since uranium was found in the ZrC coating layers as shown in Figs. 2–4, the reaction of ZrC with UO_2 was

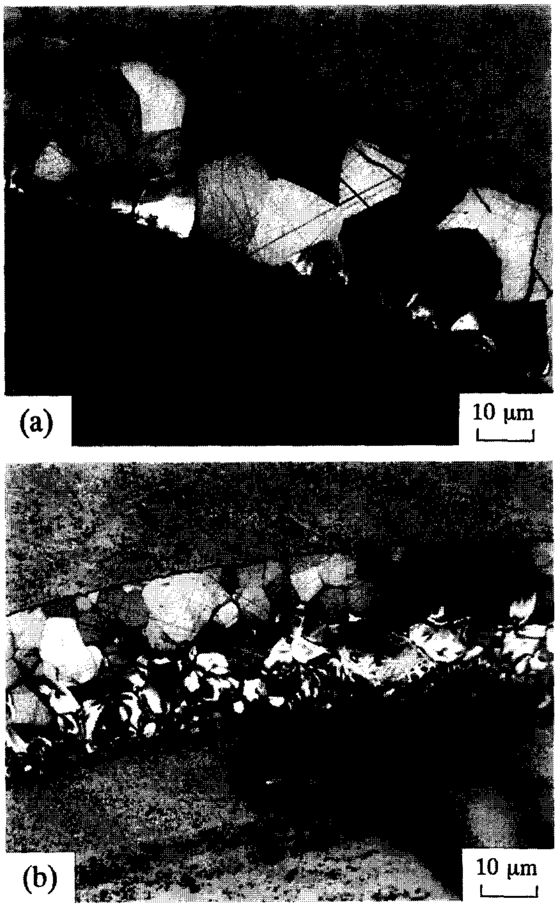

Fig. 5. Optical micrographs of etched cross section of irradiated ZrC–Triso-coated fuel particles after heating at 1800°C for 3000 h; (a) with intact IPyC coating layer and (b) with failed IPyC coating layer.

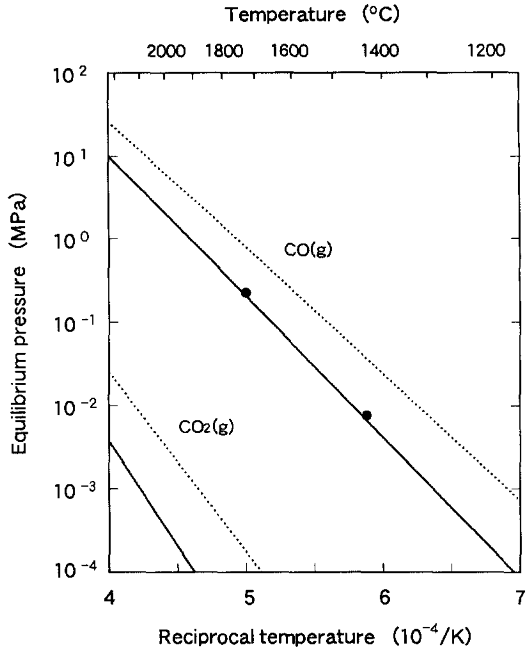

Fig. 6. Calculated equilibrium CO and CO_2 pressures in the reaction of ZrC with CO (solid lines), together with those of SiC with CO (dotted lines) for comparison. Solid circles represent the calculated results from Ref. [22].

analyzed secondly. It was found that ZrC would not react with UO_2 although it would react with CO(g) under the specified conditions. This result was supported by the heating experiment of the intimate mixture of ZrC and UO_2 in vacuum at 1700°C, where no reaction of ZrC with UO_2 was found [24].

Table 3
Species considered in the thermodynamic analysis

Species (Ref.)				
Gaseous species				
O_2 [18]	O [18]	CO [18]	CO_2 [18]	C_2O [18]
C [18]	C_2 [18]	U [18]	UO [19]	UO_2 [19]
UO_3 [19]	Zr [18]	ZrO [18]	ZrO_2 [18]	Si [18]
Si_2 [18]	Si_3 [18]	SiO [18]	SiO_2 [18]	SiC [18]
Si_2C [18]	SiC_2 [18]			
Condensed species				
UO_2 [19]	C [18]	ZrC [18]	ZrO_2 [18]	SiC [18]
SiO_2 [18]				

According to the thermodynamic analysis, ZrC would

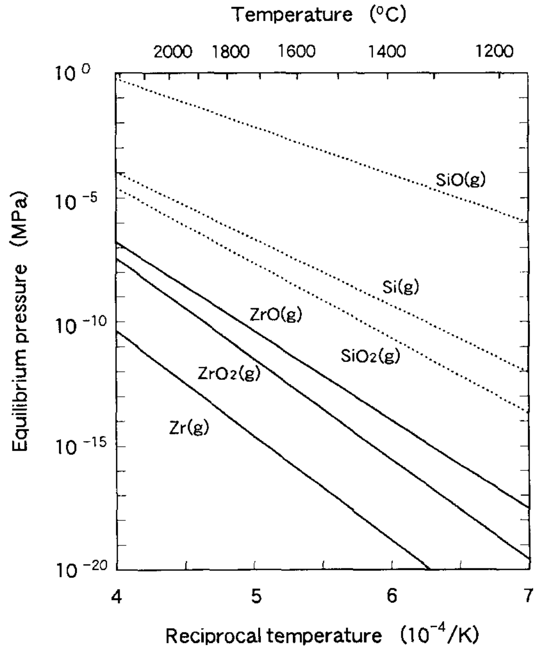

Fig. 7. Calculated equilibrium partial pressures of main gaseous species in the reaction of ZrC with CO, together with those of SiC with CO for comparison.

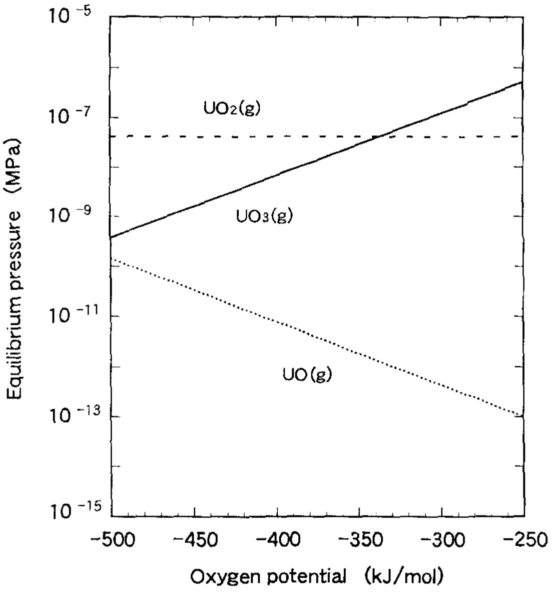

Fig. 8. Calculated equilibrium partial pressures of UO_3, UO_2 and UO as a function of oxygen potential at 1800°C.

react with $UO_3(g)$ to form ZrO_2, UO_2 and C. Fig. 8 compares the equilibrium partial pressures of $UO_3(g)$, $UO_2(g)$ and UO(g) in the fuel kernel at 1800°C as a function of oxygen potential. The pressure of $UO_3(g)$ was found to be higher than that of $UO_2(g)$ at the oxygen potentials above −340 kJ/mol at 1800°C. However, the oxygen potential of the present ZrC–Triso-coated fuel particles was roughly estimated to be about −400 kJ/mol at 1800°C on the basis of the results of the previous thermodynamic calculation [20]. This indicated that the pressure of $UO_3(g)$ was about 10% of that of $UO_2(g)$ in the present case.

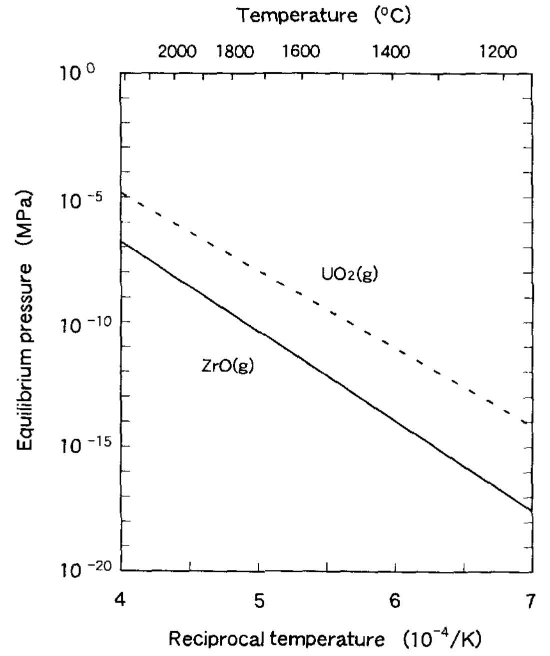

Fig. 9. Calculated equilibrium partial pressures of main gaseous species of ZrO and UO_2 in the reaction of ZrC and UO_2 with CO.

The equilibrium partial pressures of ZrO(g) and $UO_2(g)$ are compared as a function of temperature in Fig. 9, where it is seen that the $UO_2(g)$ pressure is, by more than two orders of magnitude, higher than the ZrO(g) pressure.

4. Mechanism of deterioration

Based on the results of the ceramography and electron probe microanalysis, together with those of the thermodynamic analysis, the following mechanism of the deterioration of the ZrC–Triso-coated fuel particles at 1800 to 2000°C is proposed:

1. Failure of the IPyC coating layer.
2. Exposure of the ZrC coating layer to CO(g).
3. Reaction of the ZrC coating layer with CO(g) to form ZrO_2 and C.
4. Loss of the retentivity of fission products by the ZrC coating layer.

According to the ceramography and electron probe microanalysis, the failure of the IPyC coating layer probably occurred mechanically. The irradiation-induced shrinkage of the IPyC coating layer causes tensile stresses to the layer [25]. The pressure of CO(g) and gaseous fission products in the particle also causes tensile stresses to the IPyC coating layer. For example, the pressure in the coated fuel particle with 3.6% FiMA would be about 40 MPa at 2000°C [21], which of course depends on the burnup and the dimensions of the coated particle.

Besides the failure of the IPyC coating layer, the loss of the gastightness of the IPyC coating layer makes the ZrC coating layer exposed to CO(g). The ZrC–Triso-coated fuel particle shown in Fig. 1(a) may be a good example of the deterioration caused by a gas-permeable IPyC coating layer. Gas-permeability of the PyC coating layer depends on the deposition conditions [26,27].

The thermodynamic analysis showed that the ZrC coating layer would react with CO(g) to form ZrO_2 and C when the IPyC coating layer is failed. The ceramography and electron probe microanalysis revealed the presence of carbon in the reaction zone of the ZrC coating layer, which may be the reaction product predicted by the thermodynamic analysis. The presence of zirconium in the fuel kernel observed must be attributed to the mass transfer through vapor phase of ZrO(g). The presence of uranium in the ZrC coating layer must also be attributed to the vapor phase transfer through either UO_2 (g) or $UO_3(g)$. In the case of $UO_2(g)$, only condensation of the gaseous species occurs at the reaction zone of the ZrC coating layer. The possibility of the reaction of ZrC with $UO_3(g)$ may be small due to the low vapor pressure of $UO_3(g)$.

The reaction of the ZrC coating layer with CO(g) would lead to the loss of retentivity of fission products. The ceramography showed the morphology change of the ZrC coating layer, which probably corresponds to the loss of retentivity.

Although ZrC itself is stable up to the eutectic point with carbon at 2850°C, the deterioration of the ZrC–Triso-coated fuel particles was observed at 1800 to 2000°C. This deterioration was caused by the failure of the IPyC coating layer, as mentioned above. The ZrC coating layer would be intact when the IPyC coating layer is intact. Therefore, a way to improve the high temperature stability of the ZrC–Triso-coated fuel particle is to avoid exposing the ZrC coating layer to CO(g). The properties of the IPyC coating layer at high temperatures may be improved by adequate deposition conditions. Appropriate thickness of the coating layers and diameter of the fuel kernel may improve the stability of the IPyC layer.

5. Conclusions

To understand the mechanism of the deterioration of the ZrC–Triso-coated fuel particles at 1800 to 2000°C, the ceramographic examination and the electron probe microanalysis were performed on the ZrC–Triso-coated fuel particles after the post-irradiation heating tests, and the thermodynamic analysis of the Zr–C–U–O system was carried out. The following was concluded.

(1) The thermodynamic analysis showed that the ZrC coating layer would react with CO(g) to form ZrO_2 and C when the IPyC coating layer is failed. The results of the ceramographic examination and the electron probe microanalysis were consistent with those of the thermodynamic analysis.

(2) Based on the results of the ceramographic examination, the electron probe microanalysis and the thermodynamic analysis, the mechanism of the deterioration of the ZrC–Triso-coated fuel particles was proposed. The deterioration of the ZrC–Triso-coated fuel particles observed at 1800 to 2000°C was caused by the failure of the IPyC coating layer.

(3) A way to improve the high temperature stability of the ZrC–Triso-coated fuel particle is to avoid exposing the ZrC coating layer to CO(g) produced by the reaction of the buffer layer with the liberated oxygen from uranium dioxide during fission.

Acknowledgements

The authors wish to express their thanks to Dr T. Ogawa, Department of Chemistry and Fuel Research, Japan Atomic Energy Research Institute, for his technical advice and helpful discussion. Thanks are also due to Dr M. Hoshi, Director of the department, for his interest and encouragement, and colleagues in the Department of JMTR Project for their cooperation in the irradiation test.

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