ELSEVIER

Journal of Nuclear Materials 246 (1997) 215–222

journal of nuclear materials

Advanced coatings for HTGR fuel particles against corrosion of SiC layer

Kazuo Minato [a,*], Kousaku Fukuda [a], Akiyoshi Ishikawa [b], Naoaki Mita [b]

[a] *Department of Chemistry and Fuel Research, Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki-ken 319-11, Japan*
[b] *Department of Hot Laboratories, Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki-ken 319-11, Japan*

Received 12 February 1997; accepted 14 April 1997

Abstract

For fuel particles of the high-temperature gas-cooled reactors, three types of new combinations of the coating layers were invented to prevent the corrosion of the SiC layer by fission products. The idea was that a layer to trap fission products was added inside the SiC layer of the Triso-coating. Two kinds of materials of SiC and SiC with free carbon were selected as additional layers. The fuel particles with these advanced coatings were fabricated to test the effectiveness of the coatings in out-of-reactor and irradiation experiments. These experiments showed that the advanced coatings had good irradiation performance and functioned effectively against corrosion of the SiC layer, although further irradiation tests are needed to completely demonstrate the effectiveness of the advanced coatings. © 1997 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 fuel elements. The Triso-coated fuel particles are to be used in current HTGR designs [1–3]. The Triso-coated fuel particles consist 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). Fig. 1 shows an optical micrograph of the polished cross-section of a Triso-coated fuel particle. 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 during irradiation and protects the fuel kernel from the reaction with the coating gases during the SiC coating process. 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.

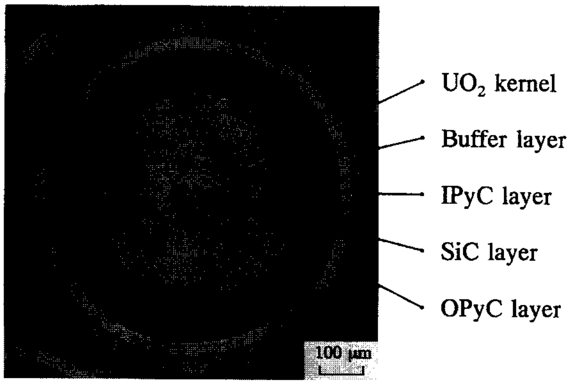

Fig. 1. Optical micrograph of the polished cross-section of the Triso-coated fuel particle.

Chemical interaction of the SiC coating layer with fission products is one of the possible performance limitations of the Triso-coated fuel particles. Fission products of palladium and lanthanide are known to react with the SiC layer. Corrosion of the SiC layer could lead to fracture of

---

[*] Corresponding author. Tel.: +81-29 282 5402; fax: +81-29 282 6442; e-mail: minato@popsvr.tokai.jaeri.go.jp.

0022-3115/97/$17.00 © 1997 Elsevier Science B.V. All rights reserved.
PII S0022-3115(97)00107-4

the coating layers or provide a localized fast diffusion path, which degrades the capability of retaining fission products within the particle. The corrosion of the SiC layer by the fission product palladium has been observed in irradiated Triso-coated fuel particles with almost all kinds of fuel compositions of UO_2, UC_2, UC_xO_y, PuO_{2-x}, $3ThO_2 \cdot PuO_{2-x}$, ThO_2 and $(Th,U)O_2$ [4–10]. Fig. 2 shows an example of the corrosion of the SiC layer by palladium observed in a Triso-coated UO_2 particle irradiated to 3.8% FIMA at 1480°C. The SiC layer was attacked locally by palladium or the reaction product formed nodules at the attacked sites. The corrosion of the SiC layer by lanthanide has been observed only in irradiated Triso-coated UC_2 and UC_xO_y ($O/U \leq 1.1$) particles [11–13].

To avoid the degradation of the coating layers caused by extensive corrosion of the SiC layer, one has to limit the burnup, fuel temperature, and/or irradiation time, or

Fig. 2. Typical example of corrosion of the SiC layer by the fission product palladium in a Triso-coated UO_2 particle irradiated to 3.8% FIMA at 1480°C.

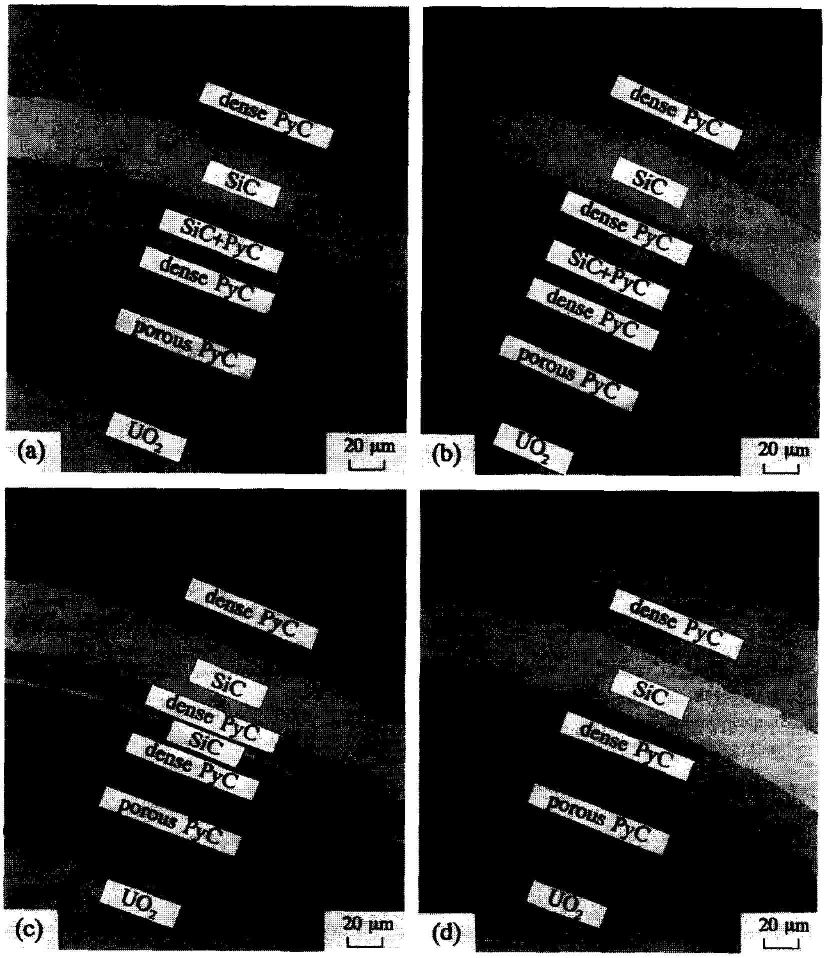

Fig. 3. Optical micrographs of the polished cross-section of the coated fuel particles; (a) type-A coating, (b) type-B coating, (c) type-C coating, and (d) Triso-coating.

increase the thickness of the SiC layer. These limitations narrow the range of choice for a design and operation of HTGR.

In the present work, new combinations of the coating layers against the corrosion of the SiC layer, especially caused by palladium, were invented, and the performance of the new coatings was tested in out-of-reactor and irradiation experiments.

2. Designs of advanced coatings

The chemical interaction of the SiC layer with fission products occurs when the fission products are released from the fuel kernel and subsequently reach the SiC layer through the IPyC layer. Generally, two methods may be available to prevent the corrosion of the SiC layer: method (a) to keep the fission products within the fuel kernel, and method (b) to make a barrier to the diffusion of the fission products to the SiC layer. The corrosion of the SiC layer by lanthanide seen in the Triso-coated UC_2 and UC_xO_y ($O/U \leq 1.1$) particles could be avoided, when the oxide or oxycarbide ($O/U > 1.1$) fuel kernels are used [11–13]. Lanthanide is kept as a stable oxide within the oxide and oxycarbide ($O/U > 1.1$). This is a typical example of method (a) mentioned above. The compositions of the fuel kernel of oxide, oxycarbide, and carbide showed, however, little effect on the corrosion of the SiC layer by palladium [4–10].

To prevent the corrosion of the SiC layer by the fission product palladium, three types of new combinations of the coating layers were invented according to method (b). The idea was that a layer, which traps palladium by chemical reaction, was added inside the SiC layer of the Triso-coating. Two kinds of additional layers were selected: a SiC + PyC layer and a SiC layer. The SiC + PyC layer is composed of SiC with free carbon [14]. This kind of layer has been studied to improve the capability of fission product retention of the dense PyC layer, as reviewed by Bullock [15].

Fig. 3 shows ceramographs of three types of advanced coatings, together with that of the Triso-coating for comparison. The type-A coating, shown in Fig. 3(a), has an additional layer of SiC + PyC adjacent to the inside of the SiC layer. As the SiC + PyC layer has a better capability of fission product retention [15], the thickness of the IPyC layer can be reduced, where the IPyC layer should act as a seal to prevent the chemical reaction of the fuel kernel during the coating process.

The type-B coating is similar to the type-A coating, as shown in Fig. 3(b), but the dense PyC layer is present between the SiC + PyC and SiC layers. The expected role of the intermediate dense PyC layer is to interrupt the radial extension of the corrosion zone from the SiC + PyC layer to the SiC layer. The corrosion zone would extend circumferentially in the SiC + PyC layer when the intermediate dense PyC layer is present. The thickness of the IPyC layer can be reduced in the same manner as the type-A coating.

In the type-C coating, SiC is used for an additional layer, as shown in Fig. 3(c). The role of the inner SiC layer is to react with fission products and the intermediate dense PyC layer is expected to interrupt the radial extension of the corrosion from the inner to outer SiC layers.

The increase in the thickness of the SiC layer of the Triso-coating may be one of the solutions to the corrosion of the SiC layer by fission products. However, the thicker coating layers will result in a smaller amount of the fuel material contained in a unit volume. With these advanced coatings, no corrosion of the SiC layer by fission products is expected to occur without increasing the total thickness of the coating layers.

3. Preparation of samples

The samples of the fuel particles with the advanced coatings were prepared for the out-of-reactor and irradiation experiments. No new technology was needed and a conventional coating apparatus without modification [14] was used to prepare the advanced coatings. This point is of great advantage to the fuel fabrication.

For the out-of-reactor experiments, three types of advanced coatings, type-A, type-B and type-C, were prepared. Since a simulated fission product of palladium was to be supplied from the outside of the particle in the out-of-reactor experiment, the coating layers were so deposited on the Triso-coated particles that the advanced coatings without the porous PyC layer were formed inside out. The porous PyC layer has little influence on the migration of palladium. For the irradiation experiments, three types of the advanced coatings, together with the Triso-coating, were deposited on the fuel kernels of UO_2 with 19.7 wt% enriched uranium, as shown in Fig. 3.

The porous PyC layer was deposited at 1300°C with the pyrolysis of acetylene (C_2H_2) in the flowing argon, and the dense PyC layer was deposited at 1365°C with the pyrolysis of propylene (C_3H_6) in the flowing argon. The density of the porous PyC layer was about 1.05 Mg/m^3, whereas that of the dense PyC was about 1.86 Mg/m^3. The SiC layer was chemically vapor deposited at 1600°C using methyltrichlorosilane (CH_3SiCl_3, MTS) and hydrogen. When the SiC + PyC layer was deposited at 1600°C, MTS and argon, without hydrogen, were used [14]. The content of free carbon in the SiC + PyC layer was about 40 wt% examined by electron probe microanalysis.

4. Out-of-reactor experiment

4.1. Experimental conditions

The coated fuel particles having the three types of the advanced coatings inside out were heated with the powder

Fig. 4. Optical micrograph of the polished cross-section of the coated fuel particle with type-A coating inside out after heating with palladium powder at 1500°C for 1 h.

of palladium at 1500°C for 1 h in the flowing argon. The purity of the palladium powder was > 99.9%. In the out-of-reactor experiment, palladium was designed to diffuse into the coating layers from the outside of the particles. Such a method was used previously by other authors to simulate the chemical interaction of the SiC layer with the fission product palladium [16–18].

The present test conditions yielded various degrees of corrosion by palladium, probably because the contact of the coated fuel particles with palladium powder was not controlled uniformly. The purpose of the present experiment was attained with these conditions, although the present test conditions were not suitable for determining the reaction rate.

4.2. Postheating examinations

The heated coated fuel particles were embedded in epoxy resin and polished to the equator of the particles of which cross-section was examined with an optical microscope. Typical examples of the optical micrographs of the heated coated fuel particles are shown in Figs. 4–6.

In the type-A coating, palladium, coming from the outside of the particle, was trapped by the SiC + PyC layer, as shown in Fig. 4. The corroded parts were seen as white spots in the second layer from the outside. No corrosion was found in the SiC layer. As expected, the SiC + PyC layer functioned well as a barrier to the diffusion of palladium to the SiC layer.

The same trap behavior of the SiC + PyC layer as observed in the type-A coating was seen in the type-B coating, as shown in Fig. 5(a). The type-B coating has the intermediate dense PyC layer between the SiC + PyC and

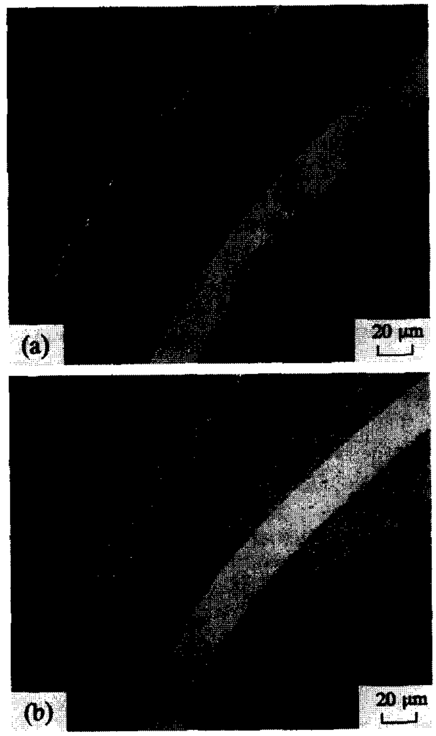

Fig. 5. Optical micrographs of the polished cross-section of the coated fuel particles with type-B coating inside out after heating with palladium powder at 1500°C for 1 h.

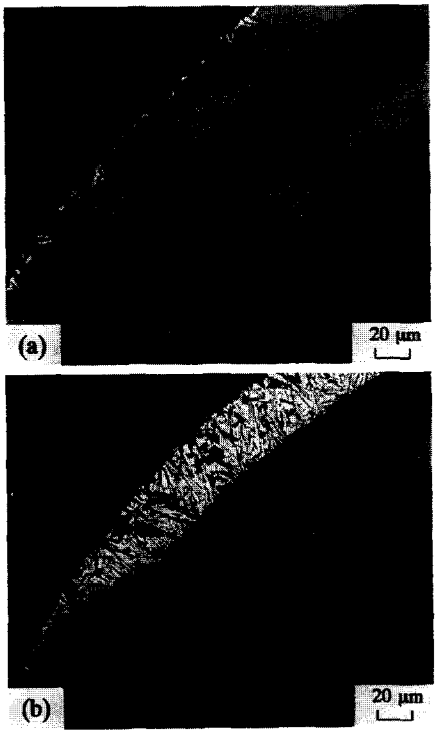

Fig. 6. Optical micrographs of the polished cross-section of the coated fuel particles with type-C coating inside out after heating with palladium powder at 1500°C for 1 h.

SiC layers. Fig. 5(b) shows the effect of the intermediate dense PyC layer on the extension of the corrosion zone. The lower part of the SiC + PyC layer seen in Fig. 5(b) was completely attacked through the coating thickness by palladium, while no corrosion was found in the SiC layer. The upper part of the SiC + PyC layer was partly corroded. This interruption of the radial extension of the corrosion zone from the SiC + PyC layer to the SiC layer was exactly the expected role of the intermediate dense PyC layer.

Fig. 6(a) shows localized corrosion of the outer SiC layer by palladium in the type-C coating, which is similar to the morphology of the corrosion observed in the irradiated Triso-coated particles. The interruption of the radial extension of the corrosion zone from the outer to inner SiC layers by the presence of the intermediate dense PyC layer was also observed in the type-C coating, as shown in Fig. 6(b). The intermediate dense PyC layer between two SiC layers functioned effectively, as expected.

In the present out-of-reactor experiment, the SiC + PyC layer was proved to be effective as a barrier to the diffusion of palladium to the SiC layer, and the intermediate dense PyC layer was found to interrupt the radial extension of the corrosion zone from the barrier layer to the SiC layer. However, it should be noted that the intermediate dense PyC layer could not interrupt the radial extension of the corrosion zone when the amount of palladium exceeds the capacity of the barrier layer to react with palladium. Although irradiation tests are necessary to confirm the effectiveness of the advanced coatings because of the possible difference between the in-reactor and the out-of-reactor test conditions, the present out-of-reactor experiment showed that the advanced coatings were promising.

Table 1
Irradiation conditions of samples

Capsule	Time (EFPD)	Burnup (% FIMA)	Temperature (°C)
ICF-67H	141.1	3.7	1330
VOF-40H	250.1	7.0	1330

5. Irradiation experiment

5.1. Irradiation conditions

The coated fuel particles with the advanced coatings of the type-A, type-B and type-C, together with the Triso-

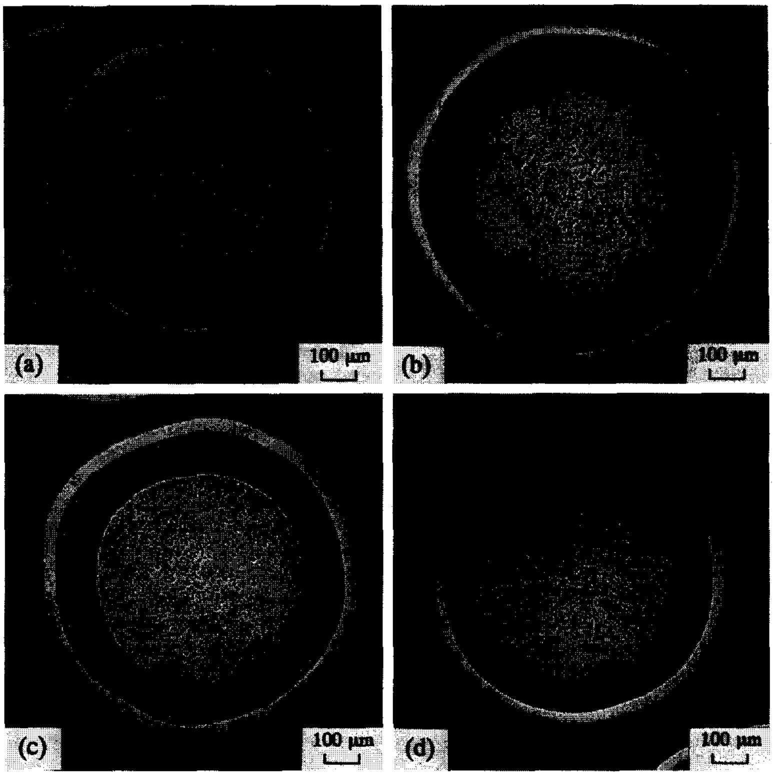

Fig. 7. Optical micrographs of the polished cross-section of the coated fuel particles after irradiation to 7.0% FIMA at 1330°C; (a) type-A coating, (b) type-B coating, (c) type-C coating, and (d) Triso-coating.

coated fuel particles, were irradiated in the Japan Research Reactor-2 (JRR-2). The sample particles were put individually into holes of graphite disks, which were piled and then loaded in two irradiation capsules. The burnups of the fuels irradiated in two capsules were 3.7 and 7.0% FIMA, respectively, which were measured by γ-ray spectrometry after irradiation. The irradiation temperature was 1330°C in both the capsules measured with thermocouples. The irradiation conditions are summarized in Table 1.

5.2. Postirradiation examinations

The irradiated coated fuel particles were examined by visual inspection, X-ray microradiography, ceramography, and electron probe microanalysis. No anomaly was found by visual inspection and X-ray microradiography.

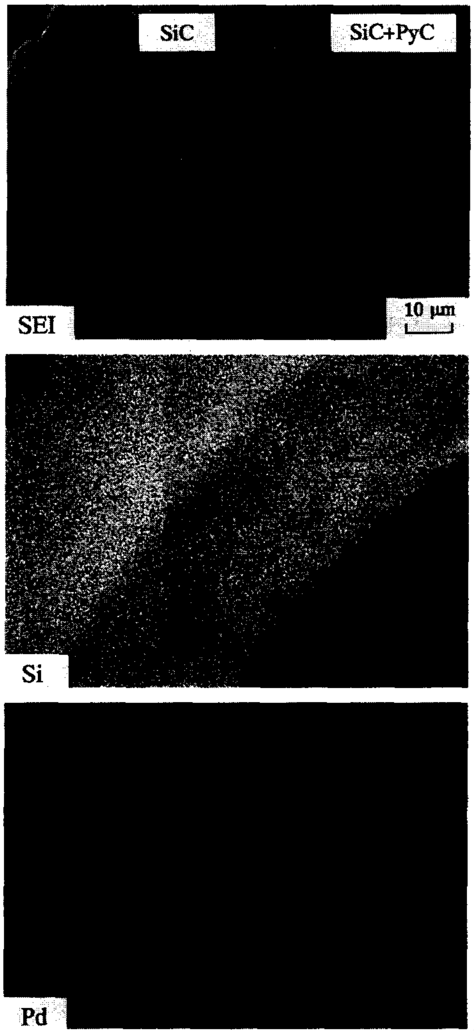

Fig. 8. Electron probe microanalysis of the polished cross-section of the coated fuel particle with type-A coating after irradiation to 7.0% FIMA at 1330°C; (a) secondary electron image, (b) X-ray image for silicon, and (c) X-ray image for palladium.

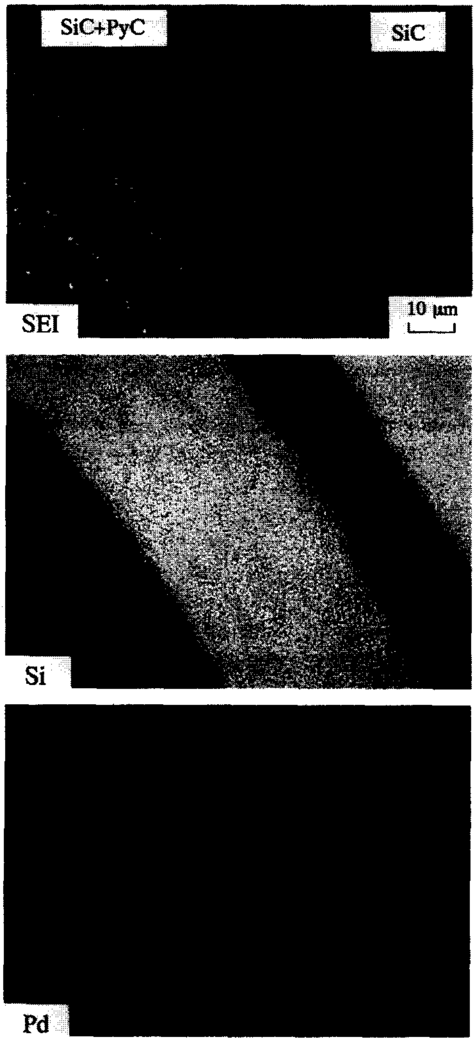

Fig. 9. Electron probe microanalysis of the polished cross-section of the coated fuel particle with type-B coating after irradiation to 7.0% FIMA at 1330°C; (a) secondary electron image, (b) X-ray image for silicon, and (c) X-ray image for palladium.

Fig. 7 shows typical examples of the optical micrographs of the polished cross-section of the coated fuel particles with three types of the advanced coatings and Triso-coating, which were irradiated to 7.0% FIMA at 1330°C. No crack was observed in the advanced coating layers as well as in the Triso-coating layers. In the advanced coatings of the type-A and type-B, the SiC + PyC layer, which is not present in the Triso-coating, showed good irradiation performance as a coating layer. The mechanical integrity of the advanced coatings was confirmed in the present irradiation experiment.

The behavior of the fission product palladium in the coating layers was examined by electron probe microanalysis. Figs. 8–11 show typical examples of the distribution of palladium in the coating layers of the type-A, type-B and type-C, together with that in the Triso-coating. Although the fission product palladium was found in the fuel kernels as metallic inclusions with molybdenum, technetium, ruthenium and rhodium, some amounts of palladium were found to be transferred from the UO_2 fuel kernel to the coating layers, as observed in previous irradiation experiments [5].

In the type-A coating, palladium was distributed along the inner surface of the SiC + PyC layer, as shown in Fig. 8. The fission product palladium released from the fuel kernel was trapped by the SiC + PyC layer and no corrosion was found in the SiC layer, as expected.

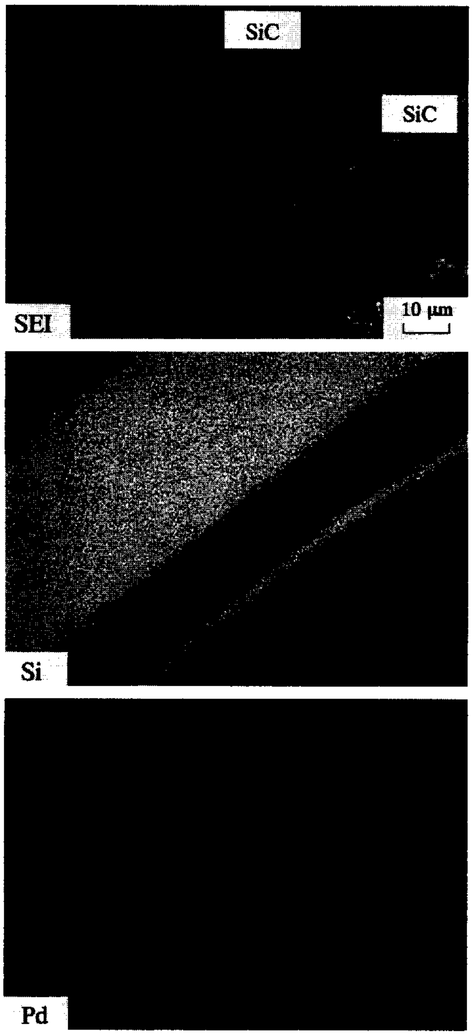

Fig. 10. Electron probe microanalysis of the polished cross-section of the coated fuel particle with type-C coating after irradiation to 7.0% FIMA at 1330°C; (a) secondary electron image, (b) X-ray image for silicon, and (c) X-ray image for palladium.

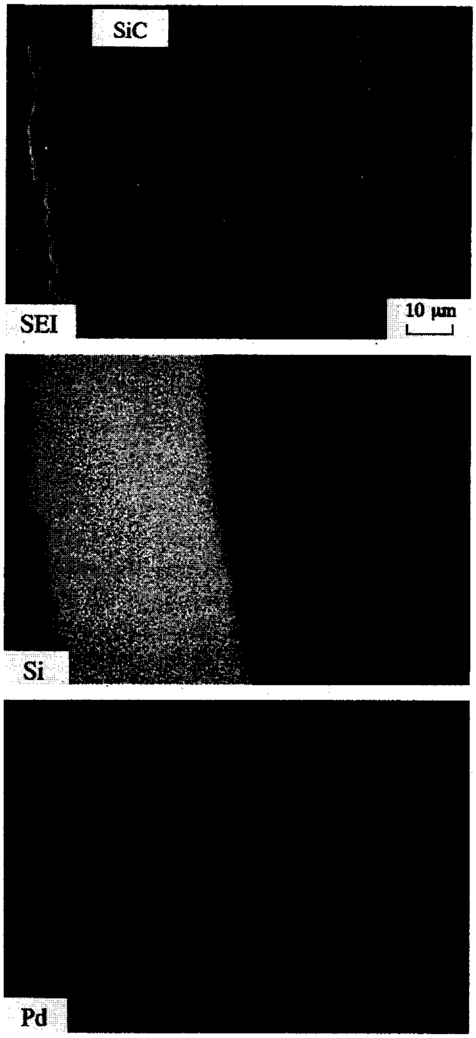

Fig. 11. Electron probe microanalysis of the polished cross-section of the coated fuel particle with Triso-coating after irradiation to 7.0% FIMA at 1330°C; (a) secondary electron image, (b) X-ray image for silicon, and (c) X-ray image for palladium.

The same behavior was also found in the type-B coating, as shown in Fig. 9. Since the corrosion depth of the coating layer by palladium was small compared with the thickness of the SiC + PyC layer, the effect of the intermediate dense PyC layer between the SiC and SiC + PyC layers on the extension of the corrosion zone could not be demonstrated in the present irradiation experiment.

In the type-C coating, palladium was found along the inner surface of the inner SiC layer, as shown in Fig. 10. The inner SiC layer trapped the fission product palladium by reacting with it. No corrosion was found in the outer SiC layer. The effect of the intermediate dense PyC layer between two SiC layers on the extension of the corrosion zone could not be demonstrated, as in the case of the type-B coating.

Fig. 11 shows the distribution of palladium in the Triso-coating. The inner surface of the SiC layer reacted with palladium.

In the present irradiation experiment, no large reaction zone of the coating layers by the fission product palladium was observed in the advanced coatings and the Triso-coating. Although further irradiation tests are needed to completely demonstrate the effectiveness of the advanced coatings, the present irradiation experiments showed that the SiC + PyC layer had good irradiation performance and the advanced coatings were effective methods against corrosion of the SiC layer by the fission product palladium.

6. Conclusions

Three types of new combinations of coating layers were invented to prevent the corrosion of the SiC layer by fission products. The idea was that a layer to trap fission products was added inside the SiC layer of the Triso-coating. Two kinds of materials of SiC and SiC + PyC were selected as additional layers. Through the fabrication, and the out-of-reactor and irradiation experiments, the following was concluded.

(1) The advanced coatings could be fabricated using a conventional coating apparatus without modification, which is of great advantage to the fuel fabrication.

(2) The advanced coatings had good irradiation performance, and the additional layers of SiC and SiC + PyC trapped palladium effectively to prevent the corrosion of the SiC layer.

(3) The intermediate dense PyC layer between the additional layer and the SiC layer was found to interrupt the radial extension of the corrosion zone from the additional layer to the SiC layer.

Acknowledgements

The authors wish to express their thanks to Dr M. Hoshi, Director of Department of Chemistry and Fuel Research, Japan Atomic Energy Research Institute (JAERI), for his interest and encouragement, and colleagues in the Department of Research Reactors, JAERI, for their cooperation in the irradiation tests.

References

[1] K. Fukuda, T. Ogawa, K. Hayashi, S. Shiozawa, H. Tsuruta, I. Tanaka, N. Suzuki, S. Yoshimuta, M. Kaneko, J. Nucl. Sci. Technol. 28 (1991) 570.
[2] H. Nabielek, W. Kühnlein, W. Schenk, W. Heit, A. Christ, H. Ragoss, Nucl. Eng. Design 121 (1990) 199.
[3] D.T. Goodin, Energy 16 (1991) 187.
[4] K. Minato, T. Ogawa, K. Fukuda, K. Ikawa, K. Iwamoto, Electron Probe Microanalysis of Irradiated Triso-Coated UO_2 Particles (II), Japan Atomic Energy Research Institute, Report JAERI-M 84-002, 1984.
[5] K. Minato, T. Ogawa, S. Kashimura, K. Fukuda, M. Shimizu, Y. Tayama, I. Takahashi, J. Nucl. Mater. 172 (1990) 184.
[6] T.N. Tiegs, Nucl. Technol. 57 (1982) 389.
[7] F. Montgomery, Fission-Product SiC Reaction in HTGR Fuel, General Atomic Company, Report DOE/ET/35300-T3, 1981.
[8] J.J. Saurwein, J.F. Holzgraf, C.M. Miller, B.F. Myers, C.F. Wallroth, Final Report on the Peach Bottom Test Element Program, General Atomic Company, Report GA-A 15999, 1982.
[9] H. Kleykamp, Mikrosondenuntersuchungen zum Verhalten der Spaltprodukte in hoch abgebrannten HTR-Brennstoffen, Kernforschungszentrum Karlsruhe, Report KfK 2213, 1975.
[10] R. Benz, R. Förthmann, H. Grübmeier, A. Naoumidis, in: Thermodynamics of Nuclear Materials 1979, Vol. I (IAEA, Vienna, 1980) p. 565.
[11] F.J. Homan, T.B. Lindemer, E.L. Long Jr., T.N. Tiegs, R.L. Beatty, Nucl. Technol. 35 (1977) 428.
[12] C.L. Smith, J. Am. Ceram. Soc. 62 (1979) 600.
[13] T.N. Tiegs, T.B. Lindemer, T.J. Henson, J. Nucl. Mater. 99 (1981) 222.
[14] K. Minato, K. Fukuda, J. Nucl. Mater. 149 (1987) 233.
[15] R.E. Bullock, J. Nucl. Mater. 113 (1983) 81.
[16] T. Ogawa, K. Ikawa, High Temp. Sci. 22 (1986) 179.
[17] T. Namba, K. Minato, M. Yamawaki, K. Fukuda, A Study on the Reaction between SiC and Pd, Japan Atomic Energy Research Institute, Report JAERI-M 87-218, 1988.
[18] T. Namba, K. Minato, M. Yamawaki, K. Fukuda, A Study on the Reaction between SiC and Pd (II), Japan Atomic Energy Research Institute, Report JAERI-M 88-267, 1989.