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**Simulated Fission Product Oxide Behavior
In Triso-Coated HTGR Fuel**

R. L. Pearson
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IN TRISO-COATED HTGR FUEL

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ABSTRACT

Several combinations of Triso-coated UO_2 particles with additions of simulated fission product oxides were investigated. They were first heat-treated in the laboratory; then their behavior was examined by metallography, radiography, the scanning electron microscope, and electron microprobe x-ray analysis. Pressures of the various gaseous species within the particles were calculated and displayed as Ellingham diagrams. It appears to be essential that Triso-coated fuel have impermeable inner high-density pyrocarbon (iLTI) layers, because the fission product strontium, in gaseous form, will interact with SiC. As oxides, the rare earth fission products redistributed slightly within the buffer layer but did not interact with the SiC layers.

1. INTRODUCTION

One of the main purposes of a SiC layer in HTGR Triso*-coated fuel particles is to serve as a barrier to prevent release of the metallic fission products.¹ Without it, many of the fission products would diffuse through the Biso[†] coating of the fuel particles² and eventually enter the primary circuit, creating a maintenance and safety hazard. Several years ago, during a postirradiation study of the behavior of metallic fission products in Triso-coated UO_2 fuel, it was noticed that the SiC layer had been attacked, and it was proposed that the attacking

*Triso is a particle-coating design consisting of a low-density pyrocarbon buffer layer, an inner high-density pyrocarbon layer (iLTI), a SiC layer, and an outer high-density pyrocarbon layer (oLTI).

[†]Biso is a particle-coating design consisting of a low-density pyrocarbon buffer layer adjacent to the kernel covered by a high-density pyrocarbon layer.

fission product was strontium.³ At about the same time, postirradiation examination of a thermal gradient annealing test of 93% enriched Triso-coated UC_2 revealed that some of the fission products had migrated down the temperature gradient to the SiC layer. In some cases there was interaction with the SiC.⁴ Electron microprobe analysis of the interaction zone revealed the presence of La, Ce, Pr, Nd, Sm, and Eu.^{4,5} These are the most abundant rare earth fission products (Table 1).⁶ It appears from these tests that interaction may occur between SiC and several fission products that exist in a specific chemical form. We have previously investigated the extent of interaction of several rare earth carbide kernels with SiC in Triso-coated particles.⁷ The purpose of this paper is to study the behavior of several simulated fission product oxides in Triso-coated particles.

Table 1. Yield summary for fission products of interest
(based on 100 fissions at thermal neutron-energy)

	^{233}U	^{235}U	^{239}Pu	^{241}Pu
Sr	12.378	9.565	3.481	2.627
Zr	32.612	31.040	18.876	15.743
Ba	6.008	6.770	6.144	6.859
La	6.311	6.385	5.681	5.881
Ce	13.114	12.183	10.566	11.385
Pr	6.536	5.838	5.289	5.028
Nd	18.182	20.640	16.217	18.781
Pm	1.710	2.229	2.050	2.392
Sm	1.327	1.833	2.883	3.671
Eu	0.125	0.193	0.535	0.800
Gd	0.019	0.022	0.245	0.423
Tb	0.001	0.001	0.021	0.049

2. EXPERIMENTAL PROCEDURE

The Triso-coated particles used in this study contained either $\text{SrO-ZrO}_2\text{-UO}_2$, SrZrO_3 , La_2O_3 , $\text{La}_2\text{O}_3\text{-LaC}_2$, $\text{Nd}_2\text{O}_3\text{-UO}_2$, $\text{Nd}_2\text{O}_3\text{-UO}_2\text{-UC}_2$, or Sm_2O_3 kernels. The oxides of the Sr-Zr-U mix were made by heating oxalates coprecipitated from nitrate solution.⁸ The concentrations of strontium and zirconium were equal to the fission yields of strontium plus barium and of zirconium, respectively, in a medium-enriched fuel (80% ^{238}U ; 20% ^{235}U) irradiated to 20% FIMA.* The resulting mixture was 1.5 wt % SrO, 3.3 wt % ZrO_2 , and 95.2 wt % UO_2 . SrZrO_3 was purchased from Alpha Products of Danvers, Massachusetts. These powders were hot-pressed, and the desired kernel sizes were obtained by crushing and sieving the pellets. Kernels of La_2O_3 , Sm_2O_3 , and the mixture of $\text{Nd}_2\text{O}_3\text{-UO}_2$ were prepared by loading a weak-acid resin (WAR-Amberlite IRC-72) with the appropriate cations from an acid-deficient nitrate solution.^{9,10} The carbonizing and partial conversion of the loaded resin to a carbide was carried out under controlled conditions.¹¹ Each batch of kernels was Triso-coated, except for the $\text{SrO-ZrO}_2\text{-UO}_2$ kernels, the oLTI layer of which was so fragile that it did not remain in place. Descriptions of the completed oxide and oxide-carbide particles are found in Table 2.

Attempts to determine the composition of the resin-loaded oxides or oxide-carbide by Debye-Scherrer x-ray patterns were unsuccessful. The patterns were too diffuse to analyze, probably because the crystallites in either the "as made" or the 2173 K heat-treated WAR particles were too small. From the x-ray pattern obtained with a scanning electron microscope (SEM), we estimated that 95% of the $\text{Nd}_2\text{O}_3\text{-UO}_2$ mixture was UO_2 . Extended hot chlorine leach tests,¹² performed prior to application of the SiC layer, revealed that all of the batches listed in Table 2 had impermeable iLTI layers, except for the SrZrO_3 particles. This conclusion was drawn because no change could be observed in radiographs taken before and after an 18-hr chlorine treatment at 1773 K and because no chlorine was detected in the SEM x-ray patterns of the completed particles. However, 5% of the SrZrO_3 kernels was removed after the chlorine treatment.

*FIMA — Fissions per Initial Heavy Metal Atoms.

Table 2. Characterization of particles containing simulated fission product oxides
for use in SiC interaction studies

Kernel composition	Batch No.	Kernel diameter (μm)	Buffer thickness (μm)	iLTI ^a thickness (μm)	SiC thickness (μm)	oLTI ^b thickness (μm)
SrO-ZrO-UO ₂	OR-2770	354-420	114	86	59	
SrZrO ₃	OR-2771	354-420	62	44	43	98
La ₂ O ₃	OR-2700	340	44	48	33	50
La ₂ O ₃ -LaC ₂	OR-2699	340	66	64	42	39
Nd ₂ O ₃ -UO ₂	OR-2696	440	121	45	41	41
Nd ₂ O ₃ -UO ₂ -UC ₂	OR-2697	440	164	33	32	45
Sm ₂ O ₃	OR-2698	385	23	34	25	38

^aiLTI = inner high-density pyrocarbon layer.

^boLTI = outer high-density pyrocarbon layer.

About 25 particles from each batch were enclosed at midplane of a 1.25-cm-diam carbon disk and heat-treated in a graphite-resistance furnace in which a known temperature and temperature gradient of 278 K/cm was maintained. The details of the procedure used to prepare particles for heat treatment have been published previously.¹³ The SiC thinning, if any, was determined from radiographs or from photomicrographs of the particles polished to midplane. Heavy metal movement within the Triso-coated particles was followed by x-ray analysis using radiography and/or the SEM.

3. DATA AND ANALYSIS

3.1 Oxides Containing Strontium and Zirconium

3.1.1 SrO-ZrO₂-UO₂

A carbon disk containing Triso-coated kernels of SrO-ZrO₂-UO₂ was heat-treated at $1910\text{ K} \leq T \leq 2200\text{ K}$ in a temperature gradient of 278 K/cm. Figure 1 is a composite of photographs showing results obtained after a 94-hr heat treatment. The interior of a typical strontium-containing Triso-coated particle is seen in the optical micrograph (Fig. 1c) of a polished particle. No Sr, Zr, or U movement from the kernel during heat treatment can be detected in either the radiographs (Fig. 1b) or by SEM x-ray analysis (Fig. 1d), nor can interaction be seen at the highly magnified interface (Fig. 1e). A second disk containing Triso-coated SrO-ZrO₂-UO₂ was heated under identical conditions for 364 hr. Again, no interaction was observed in a radiograph. The limit of detection of SiC interaction in a radiograph is 2 to 3 μm ; therefore, the maximum possible rate of SiC thinning in this sample would be $8.25 \times 10^{-3} \mu\text{m/hr}$. The point is plotted in Fig. 2.

3.1.2 SrZrO₃

A carbon disk containing Triso-coated kernels of SrZrO₃ was included in the run described in Sect. 3.1.1. After 94 hr of heat treatment, no kernel-SiC interaction was evident in the radiographs. The disk was then polished until the particles reached midplane. Several of the particles

a
RADIOGRAPH
0 hr

b
RADIOGRAPH
2136K - 94hr

c
OPTICAL MICROGRAPH
1951K - 94hr

d
SECONDARY ELECTRON
IMAGE
U Ma
X-RAYS

1951K - 94hr

e
OPTICAL MICROGRAPH
1951K - 94hr

Fig. 1. Photographic results of Triso-coated $\text{SrO-ZrO}_2\text{-UO}_2$ particles before and after heat treatment at 1951 and 2136 K for 94 hr in a temperature gradient of 278 K/cm. Photographs a, b, and c are mounted so that the cold side of the particle faces the left side of the page; the cold side in photograph d faces the right side of the page.

Fig. 2. Thinning rate of SiC for Triso-coated $SrO-ZrO_2-UO_2$ and $SrZrO_3$ particles in a temperature gradient of 278 K/cm vs reciprocal temperature. Also shown (x) is an estimate of the SiC thinning rate of a Triso-coated UO_2 particle irradiated to 4% FIMA (ref. 3).

showed localized areas where complete penetration of the SiC had occurred (Fig. 3a). Each of the interaction points was at the end of a crack that led from the kernel through the carbon layers to the SiC. Microprobe examination of the interior and the interaction zone of these particles found both strontium and zirconium in the kernels, but only zirconium in the SiC breach area. A second run in the same temperature gradient, but held at a lower temperature (1725 to 2023 K) for 260 hr, resulted in several points at which interaction occurred (Fig. 3b). Again, all the interaction zones were at the ends of cracks leading from the kernel through the carbon layers to the SiC layer. At these lower temperatures, the SiC was not breached but, instead, had been penetrated to approximately midpoint. A third run in the same temperature gradient, but held at 1473 to 1773 K for 3528 hr, showed some SiC interaction at the end of each crack leading from the kernel to the SiC layer (Fig. 3c). The thinning-rate data as a function of temperature are plotted in Fig. 2.

3.2 Rare Earth Oxides

Carbon disks containing Triso-coated particles of either La_2O_3 , $\text{Nd}_2\text{O}_3\text{-UO}_2$, $\text{Nd}_2\text{O}_3\text{-UO}_2\text{-UC}_2$, or Sm_2O_3 were heat-treated at $1850 \text{ K} \leq T \leq 2175 \text{ K}$ in a temperature gradient of 278 K/cm. The La_2O_3 wafer was removed from the holder after 232 hr, and the $\text{Nd}_2\text{O}_3\text{-UO}_2$, $\text{Nd}_2\text{O}_3\text{-UO}_2\text{-UC}_2$, and Sm_2O_3 wafers were removed after 581 hr. Figures 4, 5, 6, and 7 are composite photographs used to analyze their behavior during heat treatment. Figure 4a, a radiograph of an "as made" Triso-coated La_2O_3 particle, is typical of all the WAR Triso-coated rare earth oxide particles. The spherical kernel is surrounded first by carbon layers devoid of any heavy metals and then by an outer SiC layer. The radiographs in Figs. 4, 5, 6, and 7 show that part of the heavy metals in each kernel had relocated within the inner carbon layers during heat treatment. As shown in Fig. 4b and d, some of the La_2O_3 had deposited within the buffer layer and at the iLTI-buffer layer interface. Figure 5b and d shows that some of the uranium had moved from the $\text{Nd}_2\text{O}_3\text{-UO}_2$ kernel into the buffer layer on the cold side of the particle. There is more extensive movement of uranium in the $\text{Nd}_2\text{O}_3\text{-UO}_2\text{-UC}_2$ particle, as shown in Fig. 6a and b. The kernel

Y160001

2043K - 94 hr

1800K - 260 hr

1645K - 3528 hr

Fig. 3. Photomicrographs of Triso-coated SrZrO_3 particles that have been heat-treated at 2050 K for 94 hr, 1800 K for 260 hr, and 1645 K for 3528 hr in a temperature gradient of 278 K/cm. Photographs are mounted so that the cold side of the particle faces the top of the page. Note that each interaction occurs at the end of a crack leading from the kernel to the SiC layer.

Fig. 4. Photographic results for a Triso-coated La_2O_3 particle after heat treatment at 2134 K for 232 hr in a temperature gradient of 278 K/cm. Photographs are mounted so that the cold side of the particle faces the top of the page. Note that the lanthanum redistribution was only within the buffer layer.

RADIOGRAPH
2134K - 581hr

**SECONDARY ELECTRON
IMAGE**

**Nd La
X-RAYS**

**U Mn
X-RAYS**

2134K - 581hr

Fig. 5. Photographic results for a Triso-coated $\text{Nd}_2\text{O}_3\text{-UO}_2$ particle after heat treatment at 2134 K for 581 hr in a temperature gradient of 278 K/cm. Photographs are mounted so that the cold side of the particle faces the top of the page. Note that there was some redistribution of the uranium within the buffer layer at the cold end of the particle.

Y-159250

RADIOGRAPH
2100K-581hr

SECONDARY ELECTRON
IMAGE

U Ma
X-RAYS

2100K - 581hr

Fig. 6. Photographic results for a Triso-coated $\text{Nd}_2\text{O}_3\text{-UO}_2\text{-UC}_2$ particle after heat treatment at 2100 K for 581 hr in a temperature gradient of 278 K/cm. Photographs are mounted so that the cold side of the particle faces the top of the page. Note that the kernel has shrunk and is off-center. Uranium has redistributed toward the cold side of the particle and appears to have entered the iLTI layer.

Y-159249

RADIOGRAPH
2094K - 232hr

SECONDARY ELECTRON
IMAGE

Sm L α
X-RAYS

1918K - 581hr

Fig. 7. Photographic results for Triso-coated Sm_2O_3 particles after heat treatment at 1918 K for 581 hr and 2094 K for 232 hr in a temperature gradient of 278 K/cm. Photographs are mounted so that the cold side of the particle faces the top of the page.

appears to have shrunk and is off-center. An outline of the original kernel diameter is visible in the radiograph. This phenomenon is reminiscent of radiographs of heat-treated, Biso-coated $\text{UO}_2\text{-UC}_2$ particles.¹⁴ The uranium movement is more extensive than it was in the $\text{Nd}_2\text{O}_3\text{-UO}_2$ particles. Not only has some of it moved into the buffer layer, but it looks as though some uranium is in the iLTI layer. Metallographic examination of all the heat-treated rare earth oxide particles revealed that none of the SiC layers had been damaged (Fig. 4c and e).

3.3 Rare Earth Oxide and Rare Earth Carbide Mixture

A carbon disk was filled with Triso-coated $\text{LaC}_2\text{-La}_2\text{O}_3$ particles and heat-treated at $1850\text{ K} \leq T \leq 2175\text{ K}$ in a temperature gradient of 278 K/cm . Radiographs were taken after 41 hr. A typical SiC-La interaction is shown in Fig. 8c. The penetration depth is approximately $12\text{ }\mu\text{m}$. Both the radiograph (Fig. 8a) and the SEM x-ray photographs (Fig. 8b) verify that there has been lanthanum movement to the cold side of the particle. In comparing Figs. 4 and 8, it becomes evident that lanthanum has reached the SiC-iLTI interface in the $\text{La}_2\text{O}_3\text{-LaC}_2$ particles, where it can interact with the SiC layer. The SiC thinning rate as a function of $1/T$ for Triso-coated $\text{La}_2\text{O}_3\text{-LaC}_2$ particles is plotted in Fig. 9; it is the same as that previously measured for Triso-coated LaC_2 particles.⁷ However, in the Triso-coated La_2O_3 particles, the lanthanum has only reached the iLTI-buffer layer interface; therefore, no reaction with the SiC was observed.

4. DISCUSSION

As UO_2 undergoes fission, the solid fission products separate principally into three phases: (1) oxides that are insoluble in the remaining UO_2 , (2) oxides that are in solid solution with the UO_2 , and (3) metallic inclusions.¹⁵ Included among those oxides that can form insoluble phases are barium, strontium, and zirconium. In the presence of zirconium, the stable forms of these oxides are BaZrO_3 and SrZrO_3 . However, the composition of the insoluble phase may change as the temperature is raised. Apparently, only BaO is insoluble in UO_2 at all temperatures, while SrO

Y159248

RADIOGRAPH
2100K - 41hr

**SECONDARY ELECTRON
IMAGE**

**La La
X RAYS**

2100K - 41hr

OPTICAL MICROGRAPH
1980K - 41hr

Fig. 8. Photographic results for Triso-coated La_2O_3 - LaC_2 particles after heat treatment at 1980 K or 2100 K for 41 hr in a temperature gradient of 278 K/cm. Photographs are mounted so that the cold side of the particle faces the top of the page. Note in photographs a and b that lanthanum has penetrated the iLTI on the cold side of the particle and has reached the SiC-iLTI interface.

Fig. 9. Thinning rate of SiC for Triso-coated La₂O₃-LaC₂ particles in a temperature gradient of 278 K/cm vs reciprocal temperature. The solid lines are 90% confidence limits obtained by General Atomic Company from postirradiated, thermal-gradient annealing tests of Triso-coated UC₂ (ref. 2).

may be soluble to 20 at. % above 1575 K (ref. 16) and ZrO_2 is extensively soluble in UO_2 above 1675 K (ref. 17). The insolubility of BaO and the apparent solution of SrO over the temperature range 1473 to 1973 K have been seen, in fact, in irradiated UO_2 HTGR fuel.¹⁸

The $\text{SrO-ZrO}_2\text{-UO}_2$ and SrZrO_3 samples were used in an attempt to simulate the performance of these oxide fuel components. Strontium was chosen to simulate both strontium and barium because the literature indicates the possibility of strontium interactions with the coatings, whereas barium has never been identified in the interaction zones. Sufficient strontium was added to the UO_2 sample to equal the yields of both elements. The proportion of zirconium to strontium plus barium shown in Table 1 exceeds unity; thus, even if zirconates formed, extra ZrO_2 was available to form a solid solution in the UO_2 matrix. The lack of interaction of this $\text{SrO-ZrO}_2\text{-UO}_2$ sample with SiC (Fig. 1e) is not in agreement with postirradiation results reported by Brown et al.³ Their approximated thinning rate (Fig. 2) falls closer to the data obtained from the defective SrZrO_3 particles in this study.

Some elucidation of the behavior within the various oxide particles can be achieved by evaluation of thermodynamic data. Although many excellent tabulations of free energy are available, it is frequently more convenient to use these data in the form of diagrams of the free energy of each equilibrium ΔG° vs temperature T . Equilibrium data can be obtained from these diagrams (sometimes called Ellingham diagrams).^{19,20} Assumption of equilibrium in the present particles appears reasonable because of the extended times at very elevated temperatures. Even at the lower HTGR operational temperatures, equilibrium appears to have been achieved in irradiated ThO_2 and $\text{UO}_2\text{-UC}_2$ fuels.^{21,22} In oxide and oxide-carbide fuels, the chemical potential of oxygen (or, simply, oxygen potential) is a fundamental parameter that defines many of the equilibrium chemical species; this is

$$\mu_{\text{O}_2} = \Delta G^\circ = -RT \ln (p_{\text{O}_2}/p_{\text{O}_2}^\circ)$$

where

- R = gas constant ($\text{J} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$),
 T = temperature (K),
 p_{O_2} = oxygen partial pressure (MPa),
 $p_{\text{O}_2}^o$ = oxygen pressure in the standard state, 0.101 MPa (1.00 atm).

Figures 10 and 11 are Ellingham diagrams for the Sr-Zr-O-C and Ba-Zr-O-C systems. These are divided into three regions. For example, in region A of the strontium-containing system, where a significant p_{O_2} exists, $\langle \text{ZrO}_2 \rangle$,* $\langle \text{SrZrO} \rangle$, and $\langle \text{C} \rangle$ are in equilibrium; the vapor pressures of (Sr) and (SrO) result from the equilibria $\langle \text{SrZrO}_3 \rangle \rightleftharpoons (\text{Sr}) + (\text{O}_2) + \langle \text{ZrO}_2 \rangle$ and $\langle \text{SrZrO}_3 \rangle \rightleftharpoons (\text{SrO}) + \langle \text{ZrO}_2 \rangle$ respectively. In region B, $\langle \text{SrZrO}_3 \rangle$, $\langle \text{ZrC} \rangle$, and $\langle \text{C} \rangle$ are in equilibrium, and the vapor pressures can be calculated from the equilibria $\langle \text{SrZrO}_3 \rangle + \langle \text{C} \rangle \rightleftharpoons (\text{Sr}) + 1.5(\text{O}_2) + \langle \text{ZrC} \rangle$ and $\langle \text{SrZrO}_3 \rangle + \langle \text{C} \rangle \rightleftharpoons (\text{SrO}) + (\text{O}_2) + \langle \text{ZrC} \rangle$. In region C, where an insignificant p_{O_2} exists, $\langle \text{SrC}_2 \rangle$, $\langle \text{ZrC} \rangle$, and $\langle \text{C} \rangle$ are present, and the vapor pressure of (Sr) is obtained from the equilibrium $\langle \text{SrC}_2 \rangle \rightleftharpoons (\text{Sr}) + 2\langle \text{C} \rangle$. The pressure of (SrO) in region C can be calculated from the equilibrium $\langle \text{SrC}_2 \rangle + 1/2(\text{O}_2) \rightleftharpoons (\text{SrO}) + 2\langle \text{C} \rangle$, but it is insignificant. If SrO went into solution in UO_2 instead of forming SrZrO_3 , as it does above 1575 K, the pressures of (Sr) and (SrO) would be even less than those shown in Fig. 10, at a given oxygen potential and temperature, because its activity would be reduced. Measurements of CO content have shown that the oxygen potential in HTGR UO_2 fuel lies between -375 and -500 kJ/mole during reactor operation (Figs. 10, 11, and 12).^{21,23} According to the Ellingham plot in Fig. 10, the (Sr) pressure was about 10^{-9} MPa at -500 kJ/mole and 1560 K, where the interaction shown in Fig. 3 was observed after 3528 hr. In every case the interactions occurred at the ends of cracks through the carbon layers, which resulted in direct exposure of the SiC to the gases originating from the SrZrO_3 kernel. The cause of the cracks is unknown, but the chlorine leach test did show that some of the iLTI layers were defective; therefore, the cracks may have resulted from flaws in the iLTI layer. Interestingly, the interaction points are not temperature-gradient

* Here, $\langle \rangle$ indicates a solid species and $()$ indicates a gaseous species.

ORNL-DWG 78-17982R

Fig. 10. Ellingham diagram of the Sr-Zr-O-C system. Shaded area is the oxygen potential measured in irradiated UO_2 fuel particles (ref. 23).

ORNL-DWG 78-17983R

Fig. 11. Ellingham diagram of the Ba-Zr-O-C system. Shaded area is the oxygen potential measured in irradiated UO_2 fuel particles (ref. 23).

Fig. 12. Ellingham diagram of the La-O-C system. Shaded area is the oxygen potential measured in irradiated UO_2 fuel particles (ref. 23).

oriented; rather, they occur wherever the cracks intercept the SiC layer. In the Triso-coated $\text{SrO-ZrO}_2\text{-UO}_2$ particles heated at 2200 K for 94 hr, the iLTI layers seemed impermeable to (Sr) because we saw no interaction. The (Sr) pressure inside these particles was about 10^{-5} MPa (Fig. 10). Earlier work on the $\text{UO}_2\text{-C-N}_2$ reaction at 1975 K demonstrated that a (HCN) pressure of 10^{-6} MPa was sufficient to transport substantial amounts of carbon across a 0.02-cm gap.²⁴ Thus, the (Sr) pressure should be adequate for transport. Because the Sr-SiC interaction reported by Brown et al.³ falls closer to our SrZrO_3 data than to our $\text{SrO-ZrO}_2\text{-UO}_2$ data, it may be that their observed Sr-SiC interaction was due to a permeable or defective iLTI layer in the Triso-coated UO_2 fuel. Further efforts to verify this conclusion will be undertaken. A second set of Triso-coated particles containing SrZrO_3 will be formed, heat-treated, and examined for Sr-SiC interaction.

Comparing Figs. 10 and 11 shows that a (Ba) pressure equivalent to that for (Sr) is reached only at a higher temperature at a given oxygen potential, μ_{O_2} . Therefore, as the temperature is raised, (Sr) probably could react with SiC before (Ba).

The oxides La_2O_3 , Nd_2O_3 , and Sm_2O_3 form solid solutions with UO_2 , as do all rare earth oxides. Because there was no evidence of SiC interaction in the particles containing La_2O_3 , Nd_2O_3 , or Sm_2O_3 kernels, it is concluded that the second phase, the rare earth- UO_2 solid solution phase, will not interact with the SiC coating layer. However, $\langle\text{La}_2\text{O}_3\rangle$ will vaporize and form the gas (La_2O_2) . Thermodynamic data for (La_2O_2) ²⁵ was used to calculate a pressure of about 10^{-1} MPa at 2000 K and at an oxygen potential, μ_{O_2} , of -500 kJ/mole, as seen in Fig. 12. The transfer of lanthanum into the carbon buffer layer (Fig. 4b and d) is most likely the result of this gaseous species. Unlike (La), (La_2O_2) is apparently unable to diffuse through the iLTI layer. Although the equivalent gaseous species for the other rare earths are not listed in the thermodynamic tables, it is quite likely that each has such a gaseous form because of similar chemistry. This assumption may explain why a variety of rare earths were observed to have distributed themselves quite widely within 0 and 15% converted WAR fuel particles irradiated to 85% FIMA in HRB-9.^{26,27}

The lack of interaction with SiC in the $\text{Nd}_2\text{O}_3\text{-UO}_2\text{-UC}_2$ particles implies that an irradiated $\text{UO}_2\text{-UC}_2$ fuel will not result in SiC attack by the rare earths. In the mixed fuel, all rare earth fission products will exist as solid oxides as long as the initial UC_2 content is kept below a specified maximum value.²² The observation that no SiC interaction occurs in a Triso-coated La_2O_3 particle, while the rate of SiC thinning in a Triso-coated $\text{La}_2\text{O}_3\text{-LaC}_2$ particle is the same as was seen in a Triso-coated LaC_2 particle (Fig. 8), verifies our earlier conclusion that the presence of rare earth carbides is necessary for the rare earth-SiC reaction mechanism.⁷ Conversely, the rare earth oxides, either in solid or gaseous form, are not involved in the reaction of rare earths with SiC.

5. CONCLUSIONS

The following four conclusions are drawn from this study:

1. We observed strontium-SiC interaction in strontium- and zirconium-containing Triso-coated oxide particles only if there was direct contact between the strontium gas $[(\text{Sr})]$ and the SiC. Such conditions were achieved in particles with defective iLTI layers. No reaction occurred (even at 2200 K) when the iLTI layers were impermeable. The approximated SiC thinning rate observed by Brown et al.³ in irradiated Triso-coated UO_2 , and attributed by them to be a strontium-SiC interaction, falls close to the thinning rate we obtained in strontium- and zirconium-bearing Triso-coated oxide particles with defective iLTI layers. It is possible that their strontium-SiC interaction was the result of a permeable or defective iLTI layer in the Triso-coated UO_2 fuel.

2. No SiC interactions were observed in Triso-coated Sm_2O_3 , La_2O_3 , $\text{Nd}_2\text{O}_3\text{-UO}_2$, or $\text{Nd}_2\text{O}_3\text{-UO}_2\text{-UC}_2$, even at extreme temperatures. Each of these particles has a calculated (RE_2O_2) pressure of about 10^{-1} MPa at 2000 K. Even so, these gases apparently cannot diffuse through the iLTI layer and interact with the SiC; however, they do result in some redistribution of rare earths within the buffer layer.

3. The SiC layer thins at the same rate in Triso-coated $\text{La}_2\text{O}_3\text{-LaC}_2$ particles as in Triso-coated LaC_2 particles under the same heating

conditions. Apparently, rare earth carbides will react with SiC, but rare earth oxides will not.

4. As long as some UO_2 remains during irradiation of $\text{UO}_2\text{-UC}_2$ fuel mix, the rare earth fission products will exist only as oxides, and there will be no SiC-rare earth interaction.

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