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FISSION PRODUCT Pd-SiC INTERACTION IN IRRADIATED COATED PARTICLE FUELS

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# FISSION PRODUCT Pd-SiC INTERACTION IN IRRADIATED COATED PARTICLE FUELS

T. N. Tieg

## ABSTRACT

Silicon carbide is the main barrier to fission product release from coated particle fuels. Consequently, degradation of the SiC must be minimized. Electron microprobe analysis has identified that palladium causes corrosion of the SiC in irradiated coated particles. Further ceramographic and electron microprobe examinations on irradiated particles with kernels ranging in composition from  $UO_2$  to  $UC_2$ , including  $PuO_{2-x}$  and mixed (Th,Pu) oxides, and in enrichment from 0.7 to 93.0%  $^{235}U$  revealed that temperature is the major factor affecting the penetration rate of SiC by Pd. The effects of kernel composition, Pd concentration, other fission products, and SiC properties are secondary.

The kernel composition plays essentially no role in Pd-SiC interactions but does influence the release of the rare earth fission products. In kernels with oxygen-to-uranium ratios (O/U) less than 1.1, the rare earths are released in varying degrees, from small releases at  $O/U = 1.1$  to essentially complete releases at  $O/U = 0$ , and will reside at the inner surface of the SiC coating with the Pd accumulations. At temperatures below  $1400^\circ C$ , Pd penetrates the SiC at rates faster than the rare earths, whereas at temperatures above  $1400^\circ C$  the reverse appears to be true. At the present time there appear to be no synergistic effects of both the rare earths and Pd.

The evidence indicates that no threshold concentration is necessary for Pd penetration to begin. This is because the Pd accumulates in distinct localized "nodules" at the SiC coating, and the Pd concentration in these "nodules" is probably the same for any amount of Pd per particle. The amount of Pd in a particle influences only the number of these "nodules" that are formed at the SiC coating.

The microstructure of the SiC affects the rate of Pd penetration, but the exact correlation between microstructural features and penetration rate is still unknown. This complicated area is now one of an extensive study and in the near term presents the only visible means of limiting Pd penetration of SiC.

Although Pd penetration can occur, the integrity of the SiC and its ability to retain other volatile fission products is not in jeopardy until the penetration is at least halfway through the SiC, assuming a thickness of at least  $30 \mu m$ . For the lifetime of a High-Temperature Gas-Cooled Reactor core, which is not more than 6 years, the resulting SiC loss of integrity from Pd penetration may be serious for particles operated at temperatures greater than  $1110^\circ C$ . No loss of integrity from Pd penetration is expected for particles operated at temperatures below  $1110^\circ C$ .

## INTRODUCTION

Fuel used in High-Temperature Gas-Cooled Reactors (HTGRs) consists of microspheres of fissile or fertile material (kernels) coated with successive layers of pyrolytic carbon and silicon carbide.<sup>1</sup> Silicon carbide is the main barrier to fission product release from coated particle fuels. Consequently, any degradation of the coating must be minimized.

During the ceramographic examination of irradiated coated particles made with low-enriched uranium (LEU), which is less than 10% enriched with  $^{235}\text{U}$ , corrosion of the SiC coating was observed (Fig. 1).<sup>2,3</sup> Electron microprobe analysis identified fission product palladium (Fig. 2) as the corrosive species. In contrast to other fission products such as cesium, which accumulates uniformly, the palladium accumulates in distinct nodules

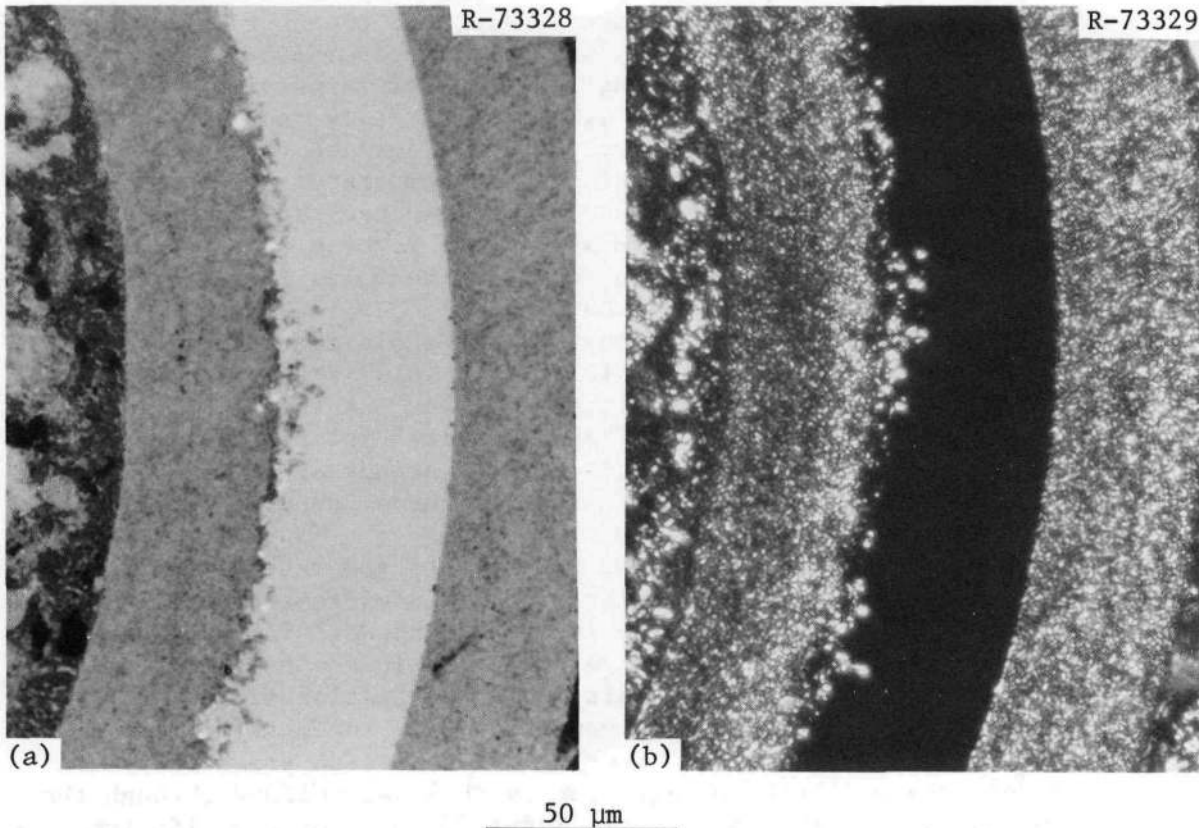
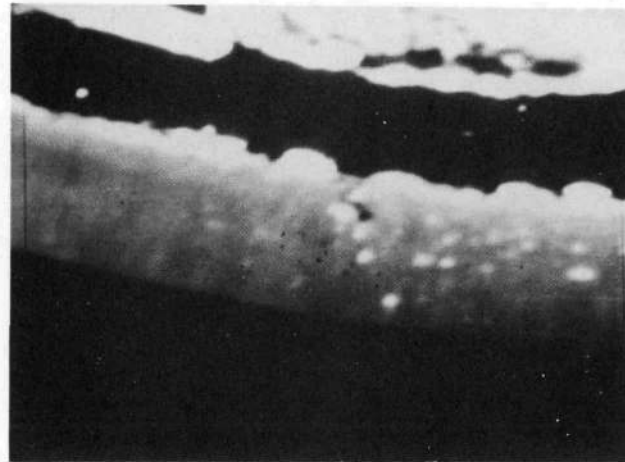


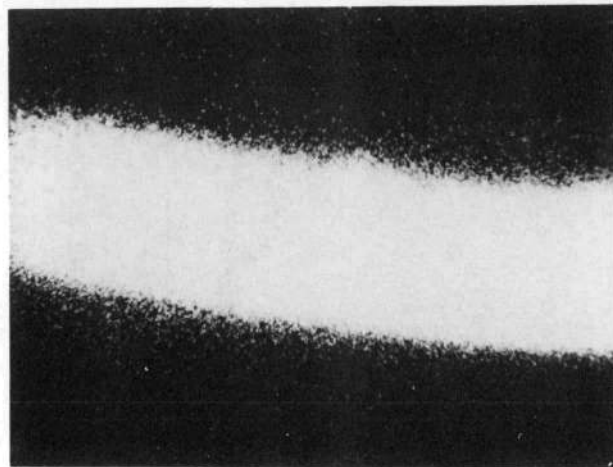
Fig. 1. High-Temperature Gas-Cooled Reactor Fuel Particles Made with Low-Enriched Uranium Showed Severe Corrosion of the SiC. (a) Bright fuel. (b) Polarized light. Irradiated in experiment HT-33 in fuel rod 19 (see Table 1) at a time-averaged irradiation temperature of 1425°C.

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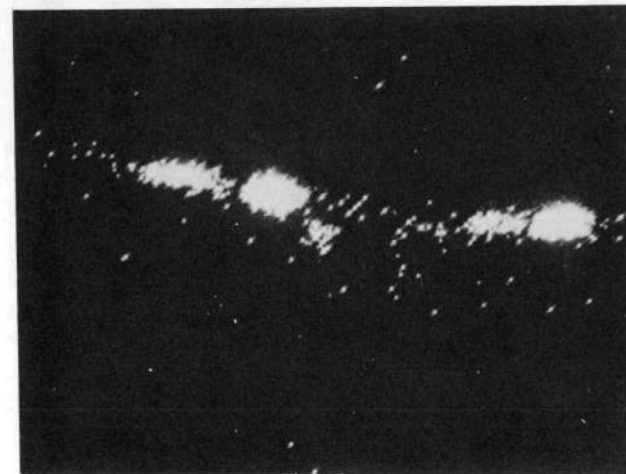
(a)

BSE IMAGE



(b)

Si  $L\alpha$



(c)

Pd  $L\alpha$

Fig. 2. Palladium was Identified as the Cause of SiC Corrosion in Low-Enriched Particles by Electron Microprobe Analysis. (a) Backscattered electron image. (b) Si  $L\alpha$  x-ray display. (c) Pd  $L\alpha$  is the same particle as shown in Fig. 1.

at the inner surface of the SiC. It has been hypothesized that the Pd penetrates the SiC along the grain boundaries where free Si is present and where Si-Pd eutectics that melt at no less than 720°C are formed. A lower concentration of Pd precedes the ceramographically visible penetration into the SiC (Fig. 3). The other fission products shown in this figure

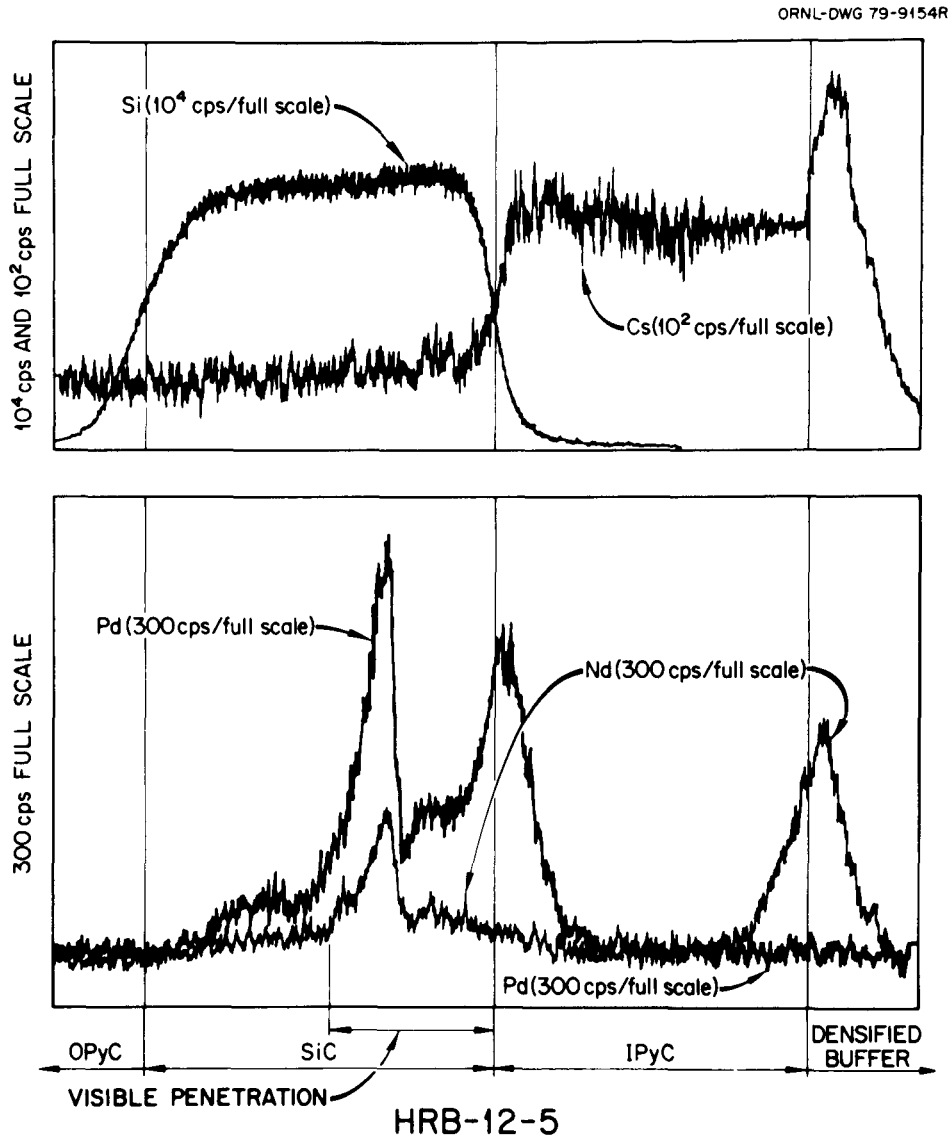


Fig. 3. Electron Microprobe Line Scans for Si, Cs, Pd, and Nd Across a Pd Penetration. A low concentration of Pd is observed ahead of visible penetration. The Nd is observed in the visible Pd accumulation (Nd is also representative of Ce, La, and Pr). The Cs is observed at the SiC inner surface but not in the Pd visible accumulation. The particle was irradiated in fuel rod HRB-12-5 (see Table 1 for irradiation conditions).



will be discussed further in the following section. While the release of Pd is of minor concern, once the SiC coating is breached, other more hazardous fission products such as  $^{137}\text{Cs}$ ,  $^{134}\text{Cs}$ , and  $^{90}\text{Sr}$  can be released from the particles.

Until these observations coated particle fuel development in the U.S. had used high-enriched uranium (HEU), which is nominally 93% enriched with  $^{235}\text{U}$ , and SiC corrosion by Pd had not been reported. This can be explained in part by the dependence of Pd production upon the fissile species. For example, the cumulative yields for the long-lived Pd isotopes from  $^{233}\text{U}$ ,  $^{235}\text{U}$ ,  $^{239}\text{Pu}$ , and  $^{241}\text{Pu}$  are 0.947, 1.609, 15.905, and 22.561%, respectively.<sup>4</sup> So with a greater proportion of Pu fissions in LEU particles than in HEU particles, the amount of Pd per particle is higher in the LEU particles. For typical cases used for the HTGRs, it has been calculated that 3.7 times more Pd would be produced in a 300- $\mu\text{m}$  kernel 20% enriched with  $^{235}\text{U}$  at a burnup of 20% fraction of initial metal atoms (FIMA) than in a 200- $\mu\text{m}$  HEU kernel at a burnup of 70% FIMA.<sup>5</sup> Thus while some Pd corrosion may have occurred in HEU fuel particles, the magnitude of such a reaction was small enough that it went unobserved. Since SiC-Pd interactions were first observed, particles with kernels ranging in composition from  $\text{UO}_2$  to  $\text{UC}_2$ , including  $\text{PuO}_{2-x}$  and mixed (Th, Pu) oxides, and in enrichment from 0.7 to 93.9%  $^{235}\text{U}$  have been examined in detail. These results are summarized in Table 1.

#### INFLUENCE OF KERNEL COMPOSITION

The kernel composition plays no direct role in Pd-SiC interactions but does affect the release of Pd and other fission products from the kernel. Obviously, if no Pd were released from the kernel, Pd corrosion of the SiC would be academic. In addition, it will be shown that other fission products released from the kernel that are entirely dependent on the kernel composition — namely the high-yield rare earths Nd, Ce, Pr, and La — do influence the behavior of Pd at the SiC coating.

In irradiated kernels of LEU dense  $\text{UO}_2$ ,  $\text{PuO}_{2-x}$ , and  $2\text{ThO}_2 \cdot \text{PuO}_{2-x}$ , some of the Pd per particle was tied up in noble metal inclusions.<sup>6,7</sup>

Table 1. Summary<sup>a</sup> of Observations on Pd-SiC Interaction in Irradiated Coated Particle Fuels at ORNL

| Experiment | Specimen <sup>b</sup> | Kernel Type <sup>c</sup>                     | 235U Enrichment (%) | SiC                          |                             |                       | Irradiation      |                     | Pd                                   |                                    |                          |
|------------|-----------------------|--|---------------------|------------------------------|-----------------------------|-----------------------|------------------|---------------------|--------------------------------------|------------------------------------|--------------------------|
|            |                       |  |                     | Density (g/cm <sup>3</sup> ) | Deposition Temperature (°C) | Coating Rate (µm/min) | Temperature (°C) | Time (h)            | Amount <sup>d</sup> (atoms/particle) | Amount (atoms/cm <sup>2</sup> SiC) | Visible Penetration (µm) |
| HRB-4      | 3A                    | WAR UC <sub>2</sub>                          | 6.0                 | 3.21                         | <i>a</i>                    | <i>a</i>              | 1200-1400        | 5,855               | 1.4 × 10 <sup>16</sup>               | 1.7 × 10 <sup>16</sup>             | ≤20                      |
| HRB-4      | 1C                    | WAR UC <sub>2</sub>                          | 6.0                 | 3.21                         | <i>a</i>                    | <i>a</i>              | 950-1100         | 5,855               | 1.5 × 10 <sup>16</sup>               | 1.8 × 10 <sup>18</sup>             | ≤0.5                     |
| HRB-5      | 3A                    | WAR UC <sub>2</sub>                          | 6.0                 | 3.21                         | <i>a</i>                    | <i>a</i>              | 1400-1600        | 3,119               | 6.3 × 10 <sup>15</sup>               | 7.5 × 10 <sup>17</sup>             | ≤0.5                     |
| HT-31      | U-17                  | Dense UO <sub>2</sub>                        | 0.7                 | 3.203                        | 1550                        | 0.25                  | <i>a</i>         | 2,147               | 2.0 × 10 <sup>16</sup>               | 8.1 × 10 <sup>17</sup>             | ≤26.5                    |
| HT-33      | 6                     | WAR UC <sub>4.40</sub> O <sub>1.43</sub>     | 7.1                 | 3.200                        | 1550                        | 0.23                  | 1150-1190        | 2,759               | 3.9 × 10 <sup>15</sup>               | 4.1 × 10 <sup>17</sup>             | 0.5-0.50                 |
| HT-33      | 19                    | WAR UC <sub>4.40</sub> O <sub>1.43</sub>     | 7.1                 | 3.200                        | 1550                        | 0.23                  | 1375-1425        | 2,759               | 5.7 × 10 <sup>15</sup>               | 5.9 × 10 <sup>17</sup>             | 5.0-18.0                 |
| HRB-11     | 2                     | WAR UC <sub>4.80</sub> O <sub>1.06</sub>     | 93.1                | 3.159                        | 1550                        | 0.41                  | 1000             | 6,559               | 2.3 × 10 <sup>15</sup>               | 3.3 × 10 <sup>17</sup>             | ≤3.0                     |
| HRB-11     | 16                    | WAR UC <sub>4.83</sub> O <sub>1.09</sub>     | 93.1                | 3.203                        | 1550                        | 0.40                  | 1250             | 6,559               | 2.9 × 10 <sup>15</sup>               | 2.8 × 10 <sup>17</sup>             | ≤7.0                     |
| HRB-11     | 21                    | WAR UC <sub>4.48</sub> O <sub>0.62</sub>     |                     | 3.194                        | 1550                        | 0.40                  | 1220             | 6,559               | 2.5 × 10 <sup>15</sup>               | 2.6 × 10 <sup>17</sup>             | ≤8.0                     |
| HRB-12     | 4                     | WAR UC <sub>4.58</sub> O <sub>1.13</sub>     | 93.1                | 3.190                        | 1550                        | 0.90                  | 1155             | 6,602               | 2.4 × 10 <sup>15</sup>               | 2.6 × 10 <sup>17</sup>             | ≤16.3                    |
| HRB-12     | 5                     | WAR UC <sub>4.60</sub> O <sub>1.10</sub>     | 93.1                | 3.197                        | 1550                        | 0.52                  | 1260             | 6,602               | 2.5 × 10 <sup>15</sup>               | 2.9 × 10 <sup>17</sup>             | ≤16.9                    |
| FTE-13     | 3,6,9,12              | Dense PuO <sub>1.81</sub>                    |                     | 3.219                        | 1500-1550                   | <i>a</i>              | 1068-1277        | 12,288 <sup>e</sup> | 1.9 × 10 <sup>15</sup>               | 1.0 × 10 <sup>18</sup>             | ≤1 <sup>f</sup>          |
| FTE-13     | 2,6,9,12              | Dense PuO <sub>1.68</sub>                    |                     | 3.202                        | 1500-1550                   | <i>a</i>              | 1091-1306        | 12,288 <sup>e</sup> | 1.2 × 10 <sup>16</sup>               | 2.3 × 10 <sup>18</sup>             | 2-12                     |
| FTE-13     | 2,6,9,12              | Dense PuO <sub>1.84</sub>                    |                     | 3.201                        | 1500-1550                   | <i>a</i>              | 1091-1306        | 12,288 <sup>e</sup> | 8.7 × 10 <sup>15</sup>               | 1.5 × 10 <sup>18</sup>             | 2-22                     |
| FTE-13     | 2,6,9,12              | Dense 3ThO <sub>2</sub> ·PuO <sub>1.69</sub> |                     | 3.216                        | 1500-1550                   | <i>a</i>              | 1069-1279        | 12,288 <sup>e</sup> | 3.0 × 10 <sup>15</sup>               | 2.7 × 10 <sup>17</sup>             | 2-4.5                    |
| FTE-13     | 2,6,9,12              | Dense 3ThO <sub>2</sub> ·PuO <sub>1.84</sub> |                     | 3.220                        | 1500-1550                   | <i>a</i>              | 1069-1279        | 12,288 <sup>e</sup> | 2.2 × 10 <sup>15</sup>               | 2.0 × 10 <sup>17</sup>             | 1-2.5                    |
| OF-2       | C-2-1                 | WAR UC <sub>5.45</sub> O <sub>1.75</sub>     | 93.1                | 3.204                        | 1550                        | 0.15                  | 1200             | 8,440               | 2.0 × 10 <sup>15</sup>               | 2.2 × 10 <sup>17</sup>             | ≤2.0                     |
| OF-2       | C-3-3                 | WAR UC <sub>4.38</sub> O <sub>0.61</sub>     | 93.1                | 3.206                        | 1550                        | <i>a</i>              | 1000             | 8,440               | 1.9 × 10 <sup>15</sup>               | 2.1 × 10 <sup>17</sup>             | ≤0.5                     |

<sup>a</sup>Values not determined are indicated with this letter.

<sup>b</sup>All specimens are rods except U-17.

<sup>c</sup>WAR - kernels derived from weak acid resins. Typically about one third of theoretical density. All other kernels have densities greater than 90% of theoretical density.

<sup>d</sup>Pd atoms per particle = [(kernel density) × (kernel volume) × (burnup) × (fission yield)/(molecular weight)] × 6.02 × 10<sup>23</sup>.

<sup>e</sup>Time in reactor = 512 effective full-power d = 12,288 h.

<sup>f</sup>Amoeba migration of kernel into SiC made accurate Pd penetration measurements impossible.

However, qualitative examination showed that the majority of the Pd per particle had been released from the kernels and resided at the SiC coating. In LEU and HEU  $UC_{xO_y}$  kernels made from low-density weak-acid resins (WARs),<sup>8</sup> no Pd inclusions or holdup by the kernel was apparent, even though other noble metal inclusions had formed in the particles with oxygen-to-uranium ratios (O/U) no less than 1.7. So with the WAR kernels all the Pd per particle will reside at the SiC coating. No observations on irradiated dense  $UC_2$  kernels were available, but thermodynamic data have indicated that Pd release from the kernel may be slowed as a result of the formation of  $UPd_3$ . However, electron microprobe analysis performed at ORNL for General Atomic Company has shown a 2- to 15- $\mu m$  Pd penetration of the SiC coating in a particle with an HEU dense  $UC_2$  kernel irradiated to a burnup of 70% FIMA (Pd =  $1.4 \times 10^{15}$  atoms/particle).<sup>10,11</sup> While the kernel was not examined in that particle, the Pd accumulations at the SiC were quite massive, and we believe that the majority of the Pd per particle resided at the SiC coating.

From these varied sources it can be inferred that, although some Pd can be held in the kernel, the majority of the Pd in a particle is released from the kernel no matter what the composition and is free to migrate to the SiC coating. In addition, the observations on the low-density WAR kernels showed that they provided essentially no holdup for Pd, whereas the dense kernels did.

Release of the high-yield rare earth fission products Nd, Ce, Pr, and La from the kernel and their migration down the temperature gradient have been commonly observed with kernels in which  $O/U \leq 1.1$ .<sup>12-14</sup> The accumulation of these rare earths at the SiC coincides exactly with the Pd accumulations (Fig. 4). Similar observations have been made with HEU dense  $UC_2$ , except that in that case the release of rare earths from the kernel was massive enough that they were not only in the Pd accumulations but were also in the surrounding area adjacent to the SiC coating. Thus, while the kernel composition has little effect on the release of Pd, it does affect the release of the rare earth fission products. The synergistic effect of Pd and the rare earths will be discussed in a following section. No other fission products accumulated with the Pd at the SiC coating.

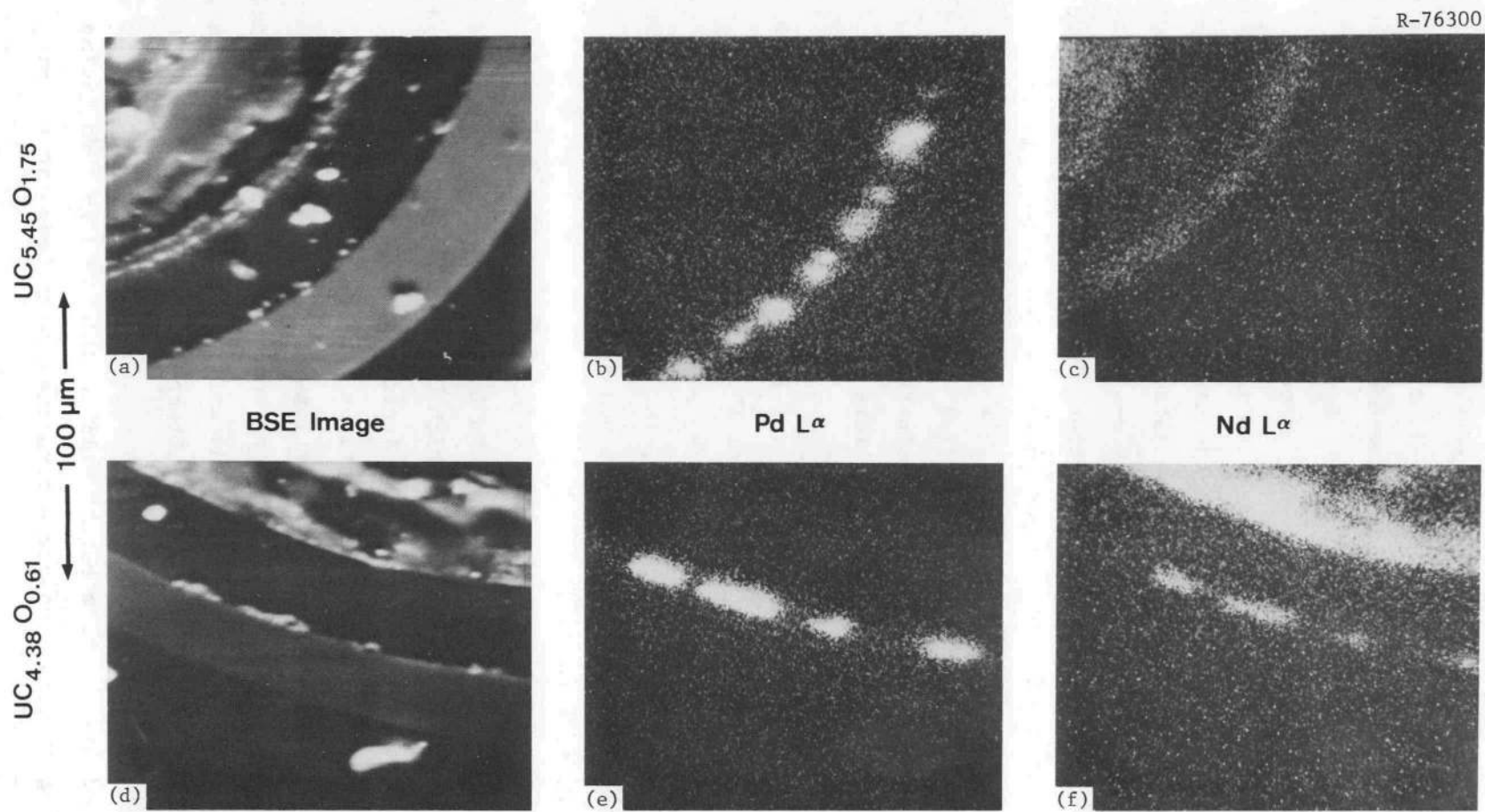


Fig. 4. Fission Product Pd and Nd Behavior at the SiC Determined by Electron Microprobe Analysis. The Nd is associated with the Pd accumulations when sufficient Nd is released from the kernel. (a) and (d) are backscattered electron images. (b) and (e) are Pd  $L\alpha$  x-ray displays. (c) and (f) are Nd x-ray displays. The Nd is representative of Ce, La, and Pr. Particle (a) was irradiated in fuel rod OF-2-C-2-1 and (d) in OF-2-C-3-3. See Table 1 for irradiation conditions.

## TEMPERATURE DEPENDENCE

Visible penetration of the SiC coating by Pd was measured on a number of ceramographically polished irradiated particles, as outlined in Table 1. In some cases the penetration was at the limit of detection of the apparatus, which is about  $0.5 \mu\text{m}$ . Although some Pd is actually ahead of the visual penetration, as shown in Fig. 3, Cs and other volatile fission products (such as the rare earths) are behind or in the visual accumulation. Therefore, it is believed that the important parameter is the visual penetration. Also the true penetration would be difficult to assess without an electron microprobe analysis of each particle. In any event, Cs release through the corrosion areas would be expected only when the visible penetration had breached the SiC. The results on the penetration rate ( $\mu\text{m}/\text{h}$ ) as a function of temperature are shown in Fig. 5.

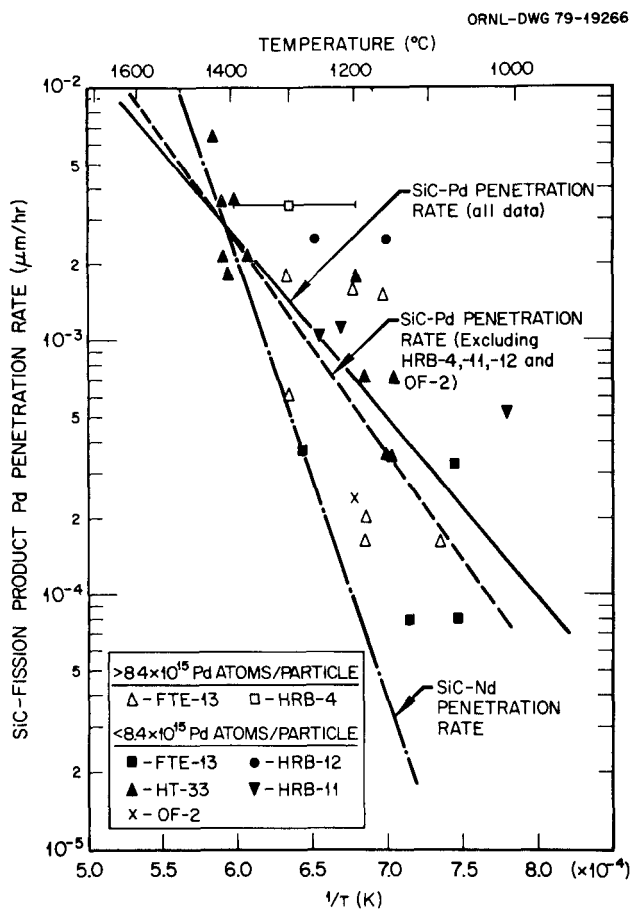


Fig. 5. The Pd Penetration Rate into SiC as a Function of Temperature.

These ceramographic observations have some error, which accounts for the scatter in the data. The major source of error stems from the examination of only one plane of polish through the particles. That plane of polish may not be truly representative of the entire particle. Therefore, the penetration distances are not truly representative, thus increasing the degree of scatter among the data points. Also contributing to the scatter of data points is the uncertainty in the temperatures. The temperatures used in the analysis represent time-weighted average temperatures, but during irradiation they can vary  $\pm 50^\circ\text{C}$  about these averages as a result of both small changes in the reactor operations and changes in the fissile fuel content of the particles.

Because of the large number of different kernel compositions examined, it should also be noted that, with the exception of the particles from irradiation tests HRB-4, -11, and -12 and OF-2, the O/U (or O/Pu) values were high enough that essentially all the rare earth fission products were retained in the kernels and thus could not contribute to any corrosion of the SiC. The penetration rate was calculated with and without the HRB-4, -11, and -12 and OF-2 data.

The penetration rate generally follows an Arrhenius relationship with temperature, that is

$$P = A \exp(-Q/RT) , \quad (1)$$

where

$P$  = rate of penetration of SiC,  $\mu\text{m}/\text{h}$ ;

$A$  = preexponential constant,  $\mu\text{m}/\text{h}$ ;

$Q$  = activation energy,  $\text{J}/\text{mol}$ ;

$R$  = gas constant,  $8.314 \text{ J}/\text{mol}\cdot\text{K}$ ;

$T$  = temperature,  $\text{K}$ .

In the present study the preexponential constant and activation energies were:

$$A = 46.2 \mu\text{m}/\text{h} ,$$

and

$$Q = 1.358 \times 10^5 \text{ J}/\text{mol} ,$$

with all data included, or

$$A = 255.2 \text{ } \mu\text{m/h} ,$$

and

$$Q = 1.599 \times 10^5 \text{ J/mol} ,$$

excluding HRB-4, -11, and -12 and OF-2 data.

As shown, the rare earths may minimally affect the activation energy associated with the Pd penetration. However, the rates described by these two equations are so close as to be indistinguishable for practical purposes (see Fig. 5) when considering the error associated with the measurements.

#### CONCENTRATION DEPENDENCE

The amount of Pd in a coated particle is a function of: (1) heavy-metal burnup and Pd yield, (2) kernel density, and (3) kernel volume. As stated previously the yield of Pd isotopes varies considerably with the fissile species and is the greatest single factor affecting the amount of Pd per particle. Thus in particles in which large percentages of the fissions were by Pu isotopes (LEU and Pu fuels) instead of by  $^{235}\text{U}$  or  $^{233}\text{U}$ , the Pd per particle will be higher for comparable heavy-metal burnups. Needless to say, concern over Pd-SiC interactions is greatest for coated particle fuels using low enrichments of  $^{235}\text{U}$ .

Corrosion of the SiC coating has been observed at all levels of Pd from  $1.9 \times 10^{15}$  to  $2.0 \times 10^{16}$  atoms/particle (Table 1). Even when considering the amount of Pd per particle on the basis of SiC surface area, penetration was observed at all levels. In Fig. 5 the data points were separated from each other based on levels of Pd greater (open points) or less than (closed points)  $8.4 \times 10^{15}$  atoms/particle. The separation point was calculated as the amount of Pd in a typical coated particle now considered for use in an HTGR. Such a particle has a 325- $\mu\text{m}$ -diam  $\text{UC}_2$  kernel, is 20% enriched with  $^{235}\text{U}$ , has a density of 10.2 Mg/m, and has a

burnup of 25% FIMA. As shown, no clear distinction between the Pd levels is evident. Therefore, no threshold amount of Pd per particle appears necessary before penetration occurs.

The Pd accumulates in distinct "nodules," so it is logical that even with low amounts of Pd per particle the concentration is high enough in localized areas to cause corrosion. It is also probable that Pd-SiC interactions went unnoticed in particles with low Pd concentrations because they are much less massive, although the penetration distances are comparable to particles with high Pd concentrations. The amount of Pd per particle directly affects the number of "nodules" formed at the SiC coating.

#### BEHAVIOR IN CONJUNCTION WITH RARE EARTH FISSION PRODUCTS

As mentioned previously the rare earths and Pd accumulations coincide with each other at the inner surface of the SiC coating for particles with kernels in which  $O/U \leq 1.1$ . It has been observed that they are also associated with each other during penetration of the SiC coating (Fig. 3).

A large body of data has been generated on the rare earth corrosion of SiC.<sup>14,15</sup> Smith<sup>14</sup> measured fission product penetration rates at temperatures no less than 1300°C on irradiated dense HEU UC<sub>2</sub> particles that had Pd levels no greater than  $1.8 \times 10^{15}$  atoms/particle. Electron microprobe analysis showed the corrosive species to be the rare earth fission products, although Pd was not mentioned or looked for as a possible contributor. Other observations on irradiated dense HEU UC<sub>2</sub> described before showed penetration of the SiC at Pd levels as low as  $1.4 \times 10^{15}$  atoms/particle. So certainly Pd should have played a role in the SiC corrosion observed by Smith.<sup>14</sup> Unfortunately no observations were made at temperatures less than 1300°C, where the majority of the present data were taken.

Pearson and Lindemer<sup>15</sup> measured rare earth penetration rates at temperatures above 1300°C on unirradiated particles that used NdC<sub>2</sub> and/or LaC<sub>2</sub> as the kernel materials. These test particles contained no Pd. The observed penetration rates by the rare earths were identical to those



described by Smith<sup>14</sup> for temperatures between 1300 and 1900°C. These results confirm the observations made by Smith<sup>14</sup> at temperatures above 1300°C and indicate that the amount of Pd per particle has very little or no effect at those temperatures.

The majority of the present results were with particles in which the rare earth fission products would not be present at the SiC coatings in any appreciable quantities to play a role in SiC corrosion, although as shown previously the rates are not greatly different. In addition, Pd was identified as the major corrosive species. These penetration rates (Fig. 5) were higher at temperatures below 1400°C than the extrapolated SiC-Nd penetration rates from refs. 14 and 15.

Thus the distinct sets of data are: (1) rare earth and Pd penetration rates at temperatures no less than 1300°C,<sup>13</sup> (2) rare earth with no Pd penetration at temperatures no less than 1300°C,<sup>15</sup> and (3) Pd with no rare earth penetration at temperatures no greater than 1400°C (our data). These data suggest that at temperatures below 1400°C, Pd penetrates the SiC at rates faster than the rare earths, whereas at temperatures above 1400°C the reverse appears to be true. Since the average temperatures in an HTGR are designed to be much less than 1400°C, Pd appears to be the more important species for further study.

#### INFLUENCE OF SiC PROPERTIES

Studies from refs. 16 through 19 have shown that the microstructure of chemical vapor deposited (CVD) SiC is dependent on the process parameters, of which the most important were deposition rate and temperature. These parameters are listed in Table 1 for the SiC coatings in this study.

Some of the data points from the range of irradiation temperatures 1155 to 1372°C with different penetration rates were selected and plotted as a function of deposition rate (Fig. 6). All the deposition temperatures were 1550°C. As shown, the penetration rate apparently decreases with deposition rate. The microstructure of the SiC with the lowest deposition rate is generally characterized by a large grain size and high density.<sup>17</sup> However, as all studies have shown, the microstructures of

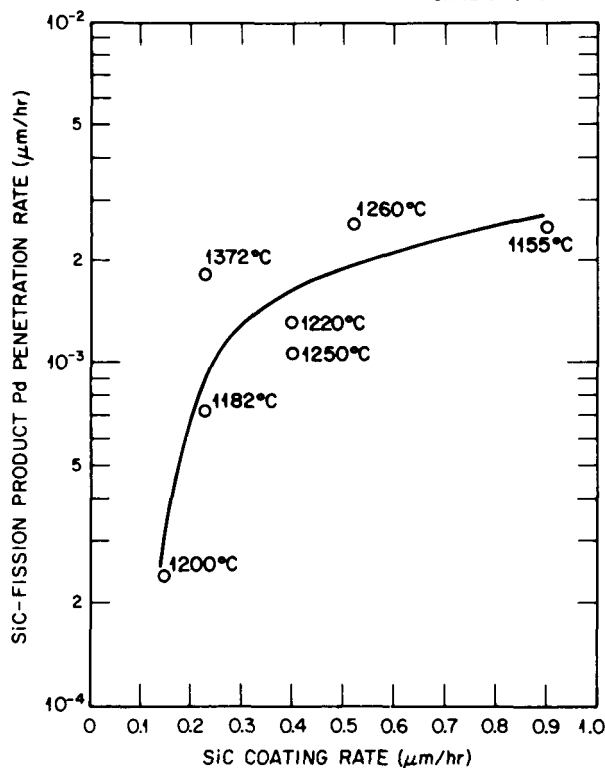


Fig. 6. Palladium Penetration Rate into SiC as a Function of SiC Coating Rate.

CVD SiC are very complex, and no one parameter is truly indicative of the microstructure on the submicroscopic level.<sup>16-19</sup> Thus, while these results are not definitive, they do indicate that the penetration rate by Pd is influenced by the microstructure of the SiC. Because these results are encouraging, efforts are now in progress to carefully examine SiC microstructures and their ability to suppress corrosion by Pd.<sup>16</sup> That study is also designed to look at suppression of fission product Ag release from SiC coated particles.

#### Pd-SiC INTERACTION IN RELATION TO SiC INTEGRITY

As shown, corrosion of the SiC coating by fission product Pd takes place in coated particle fuels. While corrosion of the SiC

coating — the main barrier to fission product release — must be minimized, the integrity of the SiC and its ability to retain other volatile fission products are the important factors.

In conjunction with the ceramographic observations on Pd penetration, gamma analysis of some coated particles was also performed. Gamma analysis has been shown to be an accurate measure of the fission product retention capabilities of coated particles by its use of the ratio of volatile to stable fission products, for example  $^{137}\text{Cs}$  to  $^{95}\text{Zr}$ .<sup>20</sup>

In capsule HT-34,<sup>21</sup> particles with kernels of LEU WAR UC<sub>4.40</sub>O<sub>1.43</sub> were irradiated at temperatures below 1370°C and in amounts of Pd less than  $6 \times 10^{15}$  atoms/particle. Gamma analysis showed that just 1 particle out of 932 examined had a significant loss of  $^{137}\text{Cs}$ . This indicates that the SiC coatings retained their integrity throughout the 2685-h irradiation. The SiC coating had Pd penetrations no more than 5  $\mu\text{m}$ . Therefore, we see that the SiC can suffer some degradation and still retain its integrity.

The extent to which the SiC can be penetrated by Pd before it loses its integrity is of concern when working with HTGR fuel particles that will be in a reactor for about 6 years. While the data is limited in this area, it has been observed that no volatile  $^{137}\text{Cs}$  loss occurred after Pd penetration 63% of the way through the SiC, that is, 26.5  $\mu\text{m}$  into a 41.8- $\mu\text{m}$  SiC<sup>6</sup> of a dense LEU UO<sub>2</sub> particle. It is probably safe to assume that this is an upper limit, especially for design purposes. The SiC coating on the particles examined was thicker than the normal 35  $\mu\text{m}$  and about 15  $\mu\text{m}$  of unpenetrated SiC remained. So for a typical particle a more conservative estimate of loss of SiC integrity would be when the penetration is just halfway through the SiC. Thus, if one calculates the Pd penetration for a particle irradiated at 1000, 1100, and 1200°C, one will see that it will be halfway through a 35- $\mu\text{m}$ -thick SiC coating in about 16.2, 6.3, and 2.8 years, respectively. The calculations also show that Pd penetration will occur halfway through a 35- $\mu\text{m}$ -thick SiC in 6 years for particles operated at 1110°C. Thus, for particles operating below 1110°C, Pd penetration should not affect the SiC integrity for the lifetime of the core. However, for those particles with temperatures above 1110°C

(it has been calculated<sup>14</sup> that less than 1% of the fuel would experience time-averaged temperatures exceeding 1250°C), Pd penetration impairing the SiC integrity is a potential problem.

#### CONCLUSIONS

Fission product Pd has been shown to corrosively penetrate the SiC in coated particle fuels. Temperature is the major factor affecting the penetration rate of SiC by Pd. The effects of kernel composition, Pd concentration, other fission products, and SiC properties are secondary.

The kernel composition plays essentially no role in Pd-SiC interactions but does influence the release of the rare earth fission products. In kernels with  $O/U < 1.1$ , the rare earths are released in varying degrees, from small releases at  $O/U = 1.1$  to essentially complete releases at  $O/U = 0$ , and will reside at the inner surface of the SiC coating with the Pd accumulations. At temperatures below 1400°C, Pd penetrates the SiC at rates faster than the rare earths, whereas at temperatures above 1400°C the reverse appears to be true. At the present time there appear to be no synergistic effects of both the rare earths and Pd.

The evidence indicates that no threshold concentration is necessary for Pd penetration to begin. This is because the Pd accumulates in distinct localized "nodules" at the SiC coating, and the Pd concentration in these "nodules" is probably the same for any amount of Pd per particle. The amount of Pd per particle influences only the number of these "nodules" that are formed at the SiC coating.

The microstructure of the SiC affects the rate of Pd penetration, but the exact correlation between microstructural features and penetration rate is still unknown. This complicated area is now one of an extensive study and in the near term presents the only visible means of limiting Pd penetration of SiC.

Although Pd penetration can occur, the integrity of the SiC and its ability to retain other volatile fission products is not in jeopardy until the penetration is at least halfway through the SiC, assuming a thickness of 30  $\mu\text{m}$ . For the lifetime of an HTGR core, which is not more than

6 years, the resulting SiC loss of integrity from Pd penetration may be serious for particles operated at temperatures greater than 1110°C. No loss of integrity from Pd penetration is expected for particles operated at temperatures below 1110°C.

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