Surface Analysis Of Uranium Dioxide Doped With Metallic ε-Particles

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Abstract

A number of surface imaging techniques are being used to investigate the size, distribution, composition and number density of noble metal ε-particles (Mo-Ru-Rh-Pd) present in simulated spent nuclear fuel (SIMFUEL). Various SIMFUEL specimens were used to mimic different degrees of simulated burn up, from 1.5 at. % to 6 at. % burn-up. Scanning electron microscopy (SEM) is being used to determine the shape and percent composition of the metal particles, and secondary ion mass spectrometry (SIMS) to determine the size and number density of the particles on the surface.

1. Introduction

The management of spent nuclear fuel is a global concern, and has been intensively researched for many years now [1-5]. One option under consideration by several countries, including Canada, is centralized containment and isolation of the used fuel in a deep geologic repository, Figure 1.

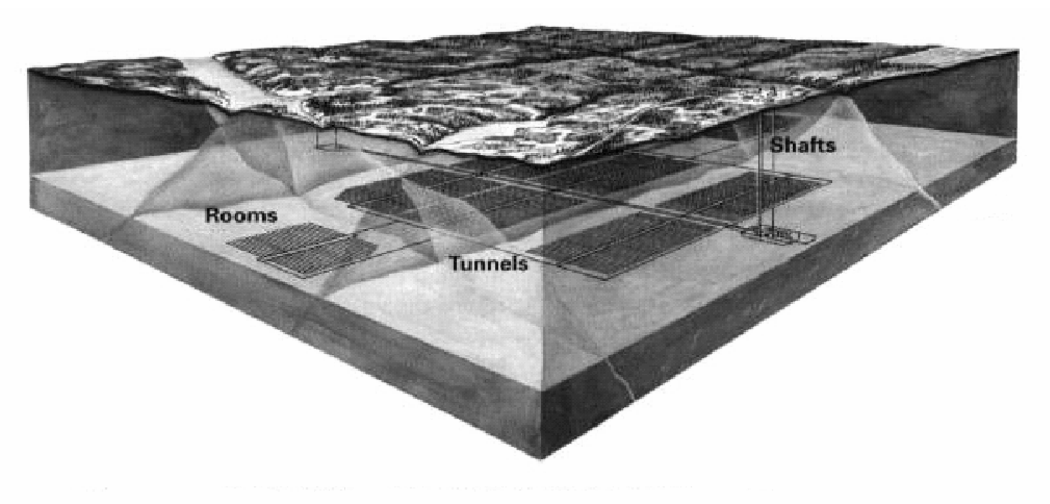

Figure 1: Artistic view of a possible Canadian nuclear waste disposal vault (www.nuclearfaq.ca).

In such a repository, the used fuel would be sealed in metallic containers and emplaced in the repository. The containers would be surrounded by compacted bentonite clay, with excess space within the repository backfilled with a mixture of clay and crushed rock. Performance assessment calculations indicate that containers, fabricated with an outer shell of copper (for corrosion protection) and an inner liner of carbon steel (for mechanical strength) should not fail by corrosion over the required disposal period [6, 7]. However, the possibility of failure due to fabrication defects remains, and considerable effort is being expended on understanding the consequences of such failures.

The study of used nuclear fuel is a great challenge, the obvious hurdle being the high radiation fields associated with spent fuel. While research on spent nuclear fuel is ongoing, the high costs and practical difficulties limit the amount of research that can be done. Also, the spent fuel available today does not mimic the fuel chemical and physical properties which will prevail if failure occurs (>10^3 years, [6, 7]). The use of non-irradiated uranium dioxide (UO_2) allows the study of nuclear fuel properties, without the limitations of cost and the high radiation energy hazard associated with it. One form of unirradiated fuel used in such studies is SIMFUEL, or simulated nuclear fuel [8, 9]. SIMFUEL mimics the chemical composition of spent nuclear fuel by doping UO_2 with a series of stable elements in the appropriate proportions to mimic in-reactor irradiation to specific levels of burnup. Many experiments have been done on SIMFUEL [10-18], and have produced results similar to those observed with spent fuel. Typically, density values ranged from 10.25 – 10.35 g/cm^3 (96.5-97.5 % of the theoretical), for a 6 at. % burnup SIMFUEL sample [8].

The chemical composition of various SIMFUEL samples has been published previously [8]. The authors of this paper prepared and investigated 3 at. % and 6 at. % SIMFUEL samples. 3 at. % SIMFUEL represents a high burnup for CANDU fuel, while 6 at. % is more representative of light water reactor fuel. While the experimental procedure for making these SIMFUEL samples are the same, variations in doping percentages were observed, and these could lead to variations in reactivity under disposal conditions.

This paper presents the results of a detailed study of the number density, size, chemical composition, and distribution of noble metal ε-particles present on the surface of various SIMFUEL samples with simulated burn-ups of 1.5 to 6.0 at. % SIMFUEL. The techniques employed were scanning electron microscopy (SEM), and secondary ion mass spectrometry (SIMS).

2. Experimental

2.1. Electrode materials and preparation

Experiments were performed on SIMFUEL electrodes cut from pellets fabricated by Atomic Energy of Canada Limited (Chalk River, Ontario, Canada). SIMFUEL is an unirradiated analogue of used nuclear fuel, produced by doping natural UO_2 with a series of stable elements (Ba, Ce, La, Mo, Sr, Y, Rh, Pd, Ru, Nd, Zr) in proportions appropriate to replicate the chemical effects of irradiation of UO_2 fuel in a CANDU reactor to various burn-ups [8, 9]. As a consequence of this doping procedure, holes are injected into the 5f band, due to the substitution of trivalent rare-earth species (e.g. Nd^{III}, Y^{III}) for U^{IV} in the UO_2 fluorite lattice, which leads to an increase in electronic conductivity. The noble metal elements (Mo, Ru, Rh, Pd), insoluble in the oxide lattice, congregate in metallic ε-particles. This phase consists of small, spherical precipitates (0.5 – 1.5 μm diameter) randomly distributed in the UO_2 matrix [8]. The SIMFUEL used in these studies mimics UO_2 fuel irradiated to 1.5, 3, or 6 at. % burn-up. As well, a SIMFUEL sample doped to 3.0 at. % but containing no ε-particles was used. The essential properties of these electrodes are listed in Table 1. The designation in Table 1 is used to refer to these electrodes in the subsequent text. Slices approximately 3 mm thick and 12 mm in diameter were cut from the SIMFUEL pellets and the electrodes prepared as previously described [16].

Table1
Properties of Electrode Materials

Designation	Material	Resistivity (ρ) (ohm·cm)
SF 1.5	1.5 at % SIMFUEL	182
SF 3.0	3.0 at % SIMFUEL	81
SF 6.0	6.0 at % SIMFUEL	1120
SS 3.0	3 at % SIMFUEL (oxides only)	174

2.2 Scanning Electron Microscopy

A Hitachi S-4500 field emission SEM was used to collect images. A high electron beam voltage of 30 kV was used resulting in a spatial resolution of < 2 nm. Micrographs were recorded at various magnifications (100 – 5000X). EDX mapping was performed to identify the size, distribution, number density, and elemental composition of ε-particles on the surface. When ε-particles were found, EDX was again performed on an individual particle to determine elemental composition.

2.3 Secondary Ion Mass Spectrometry

An ION-TOF time-of-flight secondary ion mass spectrometer (TOF SIMS IV) was used to obtain the distribution of various elements, but specifically those associated with ε-particles, in the SIMFUEL surface. A 3 keV Ar^+ ion beam was used to sputter an area of 500 x 500 μm. Once an area was sufficiently cleaned, a detailed image was taken of a 50 x 50 μm area, to show the size and number density of ε-particles on the surface.

3. Results

Figure 2 shows SIMS images for the various SIMFUEL samples with the bright spots indicating the positions of the ε-particles. The different isotopes are used to confirm the elemental composition of these particles. Rhodium is not shown in this figure since its percent abundance in the ε-particles is low at 13 percent or less of the elemental composition. This small percentage resulted in increased noise, making quantitative analysis impossible. Obvious from these images is that the average size of the particles increased with simulated burnup from sample SF1 to SF3, with the average diameter increasing from 2 μm for SF1 to 3.5 μm for SF2 and 5.1 μm with SF3. Also, the metal particles tend to cluster together with SF3, but not so much with SF1 and SF2.

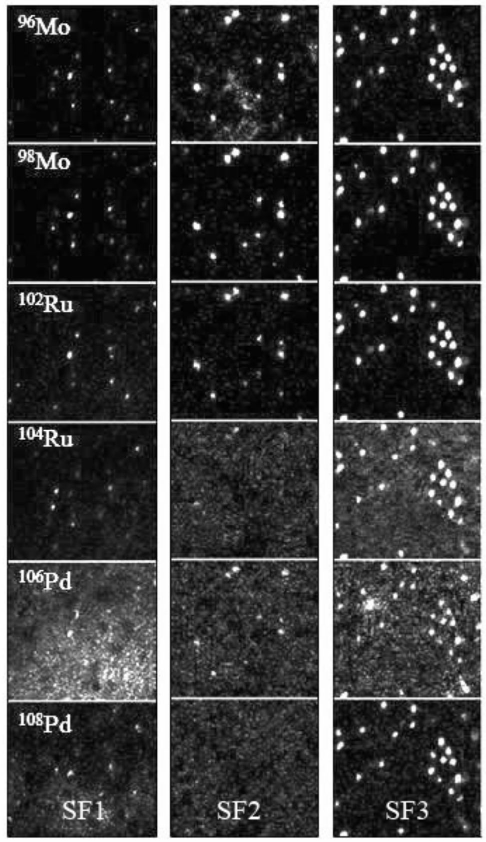

Figure 2: SIMS images showing Mo, Ru, and Pd elements. Rh is not shown due to its low concentration.

It is interesting to note the increase in size of the ε-particles with simulated burnup. Usually this is not seen with spent fuel, as the average size tends to remain around ~ 0.5 – 1.5 μm [19]. The average grain size, as seen from SEM (discussed later) remained approximately constant at 10-12 μm. This variation in size of ε-particles with burnup must be a result of the SIMFUEL fabrication process which only approximately simulates in-reactor conditions. From the SIMS images, the surface area associated with ε-particles was determined to be 1.4 % for SF1, 6.5 % for SF2 and 16 % for SF3, clearly indicating the increase in size and density with increasing burnup. While mostly uniform, SF3 did exhibit some variation in elemental composition, mainly a lower percentage of palladium was seen in several particles. Variations in ε-particle composition for SF1 could also be seen with SEM as well, and are discussed later. Another obvious trend is the number density increased with increased burnup. The average number of particles per 50 μm x 50 μm area was 9 for SF1, 15 for SF2 and 22 for SF3. The increase in number density simulates fuel behavior since increasing the burnup results in increased concentrations of fission products.

A more detailed analysis of the ε-particles was performed by SEM. Figure 3 shows an SEM image of the SF1 specimen at 2000 times magnification. The general dimensions of the image are 50 μm x 50 μm. The surface features of the SIMFUEL specimen can be observed, showing it to be rough as a result of polishing with 1200 grit sandpaper prior to imaging

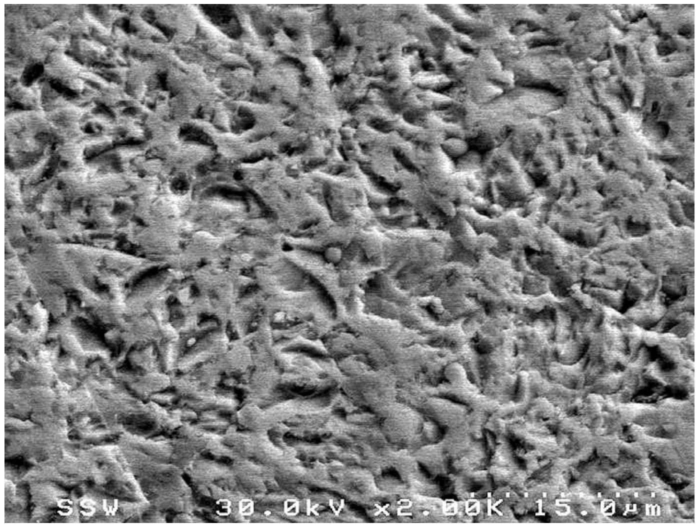

Figure 3: SEM image of SF1 at 2000 times magnification.

Since solid UO_2 is a ceramic, obtaining a finely polished surface is nearly impossible. Polishing can remove whole grains and the material possesses some void space as a consequence of the fabrication sintering process. Though hard to see on a polished sample, the grain sizes are approximately 10-12 μm in diameter. The small spherically shaped objects are ε-particles. Figure 4 shows an SEM image on SF1 showing one ε-particle. In SIMFUEL, the noble metal elements (Mo, Ru, Rh, and Pd), insoluble in the oxide lattice, congregate in metallic ε-particles, and appear uniformly distributed within the UO_2 matrix. These particles appear to be microscale solids, which differs from spent fuel, where a more porous, nano-like ε-particle structure has been observed [19]. Backscattered images were taken, but not included in this paper, and show the metal particles as darker spots on the surface, compared to the lighter UO_2 regions.

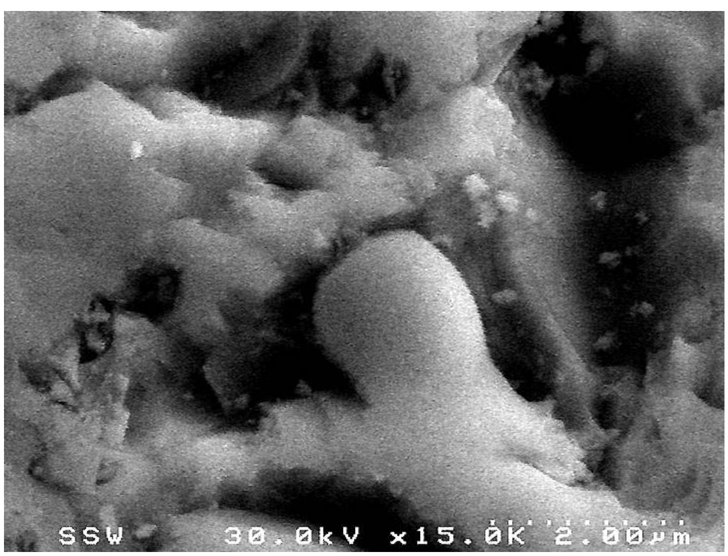

Figure 4: SEM image of SF1 at 15000 times magnification showing an ε-particle. Diameter of the ε-particle is ~ 1.5 μm.

To identify regions with ε-particles, both backscattered images and EDX mapping were performed. EDX maps were taken at 5000 times magnification, giving a rough image area of 50 μm x 50 μm. The sample was bombarded with 30 keV energy electrons, and data collected for 10 minutes, a sufficient period to observe ε-particles. This was repeated for many different areas over the entire surface. After each map, spot analyses was performed on individual particles to determine their elemental composition.

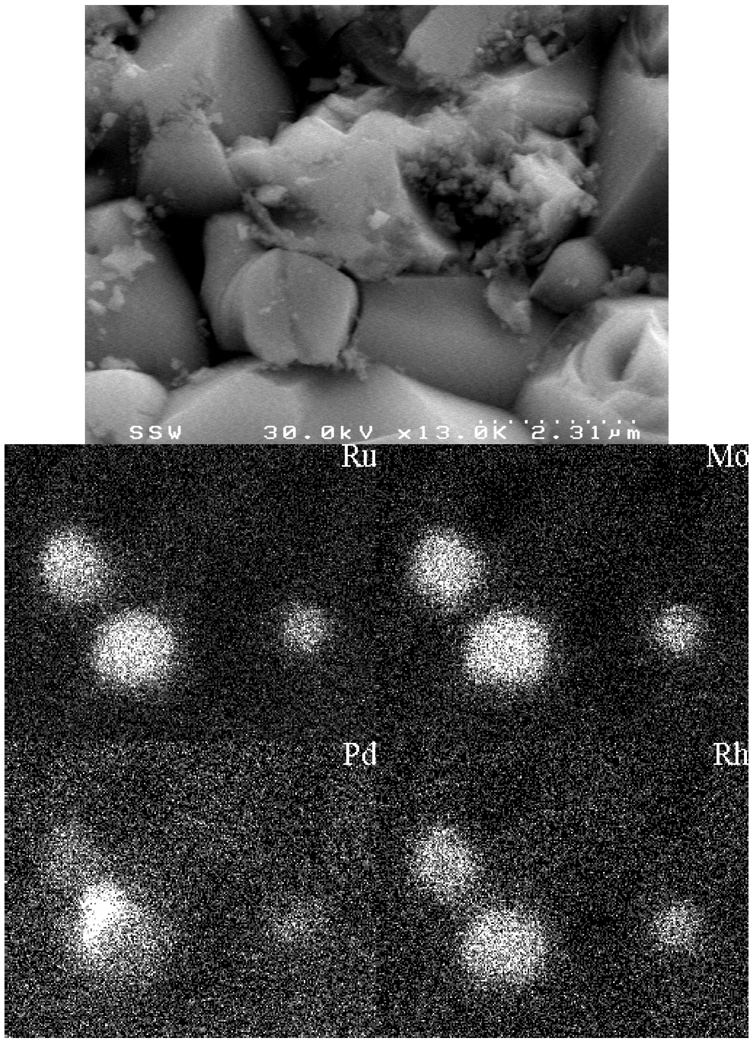

Figure 5: SEM image of SF1 showing three ε-particles (top) and an EDX map of the same area showing Ru, Mo, Pd, and Rh elements.

Figure 5 shows an EDX map for Mo, Ru, Rh, and Pd on the surface of SF1. Generally, all active spots contained all four elements, though Ru was not as concentrated in some of the particles. From similar maps for the entire UO_2 surface, the composition of individual ε-particles was determined. The average elemental composition is given in Table 2. Also listed in Table 2 is the upper and lower range found from this study. A wide variance has been found in the composition of ε-particles in spent fuel [20], but generally, our average values coincide with average values seen elsewhere [8, 20]. Average percent composition of ε-particles for CANDU spent fuel can be seen in Table 3 [20].

Table 2

Elemental composition of ε-particles with SIMFUEL sample

Designation	Pd (%)	Mo (%)	Ru (%)	Rh (%)
SF1	15.69 $\pm$ 5.00	34.75 $\pm$ 10.00	49.48 $\pm$ 12.00	0.76 $\pm$ 0.50
SF2	40.29 $\pm$ 6.00	15.56 $\pm$ 4.00	28.80 $\pm$ 5.00	13.96 $\pm$ 4.00
SF1	37.11 $\pm$ 4.00	18.59 $\pm$ 3.00	30.41 $\pm$ 5.00	13.87 $\pm$ 3.00

Table 3

Average elemental composition of ε-particles with CANDU spent fuel

Element	Pd	Mo	Ru	Rh
Average Percentage	18.2	38.1	35.2	6.5

4. Discussion

Both SIMS imaging and SEM showed a definite trend of increasing size and number density with increasing simulated burn-up. With SF6, an average of 16 % of the surface was covered with ε-particles. While this estimate may be high due to errors in constraining a minimum size for ε-particles, the percentage is still much higher than SF1, which had ~ 1.4% coverage. This increased coverage by ε-particles would be expected to lead to the more effective galvanic coupling of these particles the UO_2 matrix. This is consistent with our previous corrosion potential measurements in the presence of dissolved H_2, which indicate a strong ability of the ε-particles to act as anodes and thereby strongly inhibit fuel corrosion [16].

SEM/EDX analyses gave the average composition of ε-particles. High concentrations of Pd and Ru were found with each SIMFUEL sample. The presence of these elements should make the SIMFUEL a good catalyst for the decomposition of H_2, since they have high exchange currents for the H_2/H^+ reaction, Table 4 [21]. Rh was low in concentration with SF1, but higher with SF2 and SF3. Rh would also catalyze the H_2 decomposition reaction. Mo, however, does not have such a favorable exchange current. Mo can act like Titanium and absorb hydrogen. Since the percentage of Mo is low, it should exert a miner influence, and would not suppress the hydrogen reaction.

Table 4

Current exchange densities for the elements in ε-particles [21]

Element	Pd	Rh	Ru	Mo
Exchange Current Density ($A \cdot cm^{-2}$)	-log 3.0	-log 3.6	-log 3.3	-log 7.1

5. Conclusions

Various techniques were used to determine the size, composition, number density and distribution of noble metal ε-particles on the surface of different SIMFUEL samples. SIMS imaging showed an increase in number density and size with simulated burn-up. SEM also showed an increase in size and density, and the composition of the ε-particles was determined by EDX. The composition for SF1 sample was 15.69 % Pd, 34.75 % Mo, 49.48 % Ru, and 0.76 % Rh. Elemental compositions for SF2 and SF3 were similar to literature values.

Acknowledgements

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