Graphical Abstract

Nanostructure of Metallic Particles in Light Water Reactor Used Nuclear Fuel

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Abstract

An extraordinary nano-structure has been observed in the metallic (Mo-Tc-Ru-Rh-Pd) particles that are known to form during irradiation in light water nuclear reactor fuels. This structure points possible high catalytic reactivity through the occurrence of a very high surface area as well as defect sites. We have analyzed separated metallic particles from dissolved high burn-up spent nuclear fuel using scanning and transmission electron microscopy. The larger particles vary in diameter between ~10 and ~300 nm and possess a hexagonally close packed epsilon-ruthenium structure. These particles are not always single crystals but often consist of much smaller crystallites on the order of 1-3 nm in diameter with evidence suggesting the occurrence of some amorphous regions. It is possible that neutron irradiation and fission product recoils generated the unusual small crystallite size. The composition of the metallic particles was variable with low levels of uranium present in some of the particles. We hypothesize that the uranium may have induced the formation of the amorphous (or frustrated) metal structure. This unique nano-structure may play an important role in the environmental behavior of nuclear fuels.

1. Introduction

Light water nuclear reactor fuels used in commercial power plants consist of uranium oxide (UO_2) and/or mixed oxide (U,Pu) O_2 ceramic pellets contained within zirconium alloy cladding. The ceramic fuel possesses a high melting point (2865°C), is stable in the presence of water relative to other potential nuclear fuels and has relatively good thermal characteristics [1]. Once irradiated, the spent or used nuclear fuel becomes extremely radioactive and has undergone significant chemical changes. Many of the fission products (Zr, Sr, lanthanides) and neutron capture products (Pu, Np, and Am) are retained in the UO_2 (uraninite) fluorite-type structure. A systematic study dealing with the incorporation of lanthanides in the fluorite structure was recently reported by Horlait and co-workers [2]. A few radionuclides form new oxide phases, consisting of Cs and Ba oxides, Xe and Kr trapped as gas bubbles, and metallic inclusion forms dominated by the elements Mo, Tc, Ru, Rh, and Pd. These $4d$ series of elements all have low oxygen affinities apart from Mo, which can act as an oxygen buffer in nuclear fuels [3]. These fission product alloys have also been recognized as good hydrogen catalysts. In a spent fuel repository in a reducing environment, H_2 will be generated from the anoxic corrosion of iron. The released H_2 can become activated on the surface of the metallic fission product particles, promoting the reduction of species such as H_2O_2 and U(VI) [4]. Radioiodine has been known to move to gap regions between the ceramic and the zirconium metal cladding. However, recent work by our group (see Mausolf and co-workers) [5] indicates that it may be sequestered in an (Ag,Pd)(I,Br) phase. In this paper, we will explore analysis of the metallic residue material, commonly referred to as ‘white inclusions,’ 5-metal phases, or epsilon metal particles [6-7]. In light water reactor (LWR) fuels, the fission products Mo, Tc, Ru, Rh and Pd dominate the metallic inclusions. Other elements, including Ag, Te, Sb, Cd, In, and Sn possess oxygen

1 potentials which are also higher than that of UO_2 . Hence, these elements should also exist as
2 metals in irradiated oxide fuels. The centerline temperatures of LWR fuels do not exceed
3 1200°C , whereas, the rim regions may only reach $400\text{-}500^\circ\text{C}$. However, larger sized metallic
4 particles would not be expected to form given these fuel temperatures. The oxygen activity in the
5 oxide fuel phase increases with burn-up as fission products with valences <4 are generated. This
6 can lead to a decrease of metallic Mo and the formation of MoO_2 . The zirconium-based cladding
7 also acts as a sink for O [6-8].

8 Metallic inclusions were first identified by Bramman *et al.* [6] and later by Kleykamp *et al.* [3,
9 7,8] as a hexagonally close-packed metal (*hcp*), which possessed the ϵ -ruthenium structure.
10 Thomas *et al.* [9] also identified the ϵ -Ru(Mo,Tc,Rh,Pd) metal and fission gas bubbles in a series
11 of light water reactor fuel types with transmission electron microscopy (TEM). No other
12 elements have been reported in these particles apart from the $4d$ metal. These post-irradiation
13 examinations have been reported by Guenther and co-workers [10] in a series of published
14 reports that enabled these materials to be recognized as Approved Testing Materials (ATM) for
15 spent nuclear fuel research.

16 The Mo, Tc, Ru, Rh, and Pd metal atoms were assumed to migrate through the lattice to reach
17 the grain boundaries or bubbles; however, the details of the atomic scale mechanism remain
18 elusive [11]. The metallic particles reported by Thomas *et al.* [10] observed with TEM in LWR
19 fuels with burn-ups of 44 and 48 MWd/KgU , occurred as spherical metallic particles ranging in
20 size from about 10 nm to 200 nm in diameter with a composition that was consistent with the
21 expected ratio of these fission products in the fuel. The size of the particles was dependent on
22 their location in the fuel. The largest particles were 3 to 10 μm in fuels that had reached
23 1700°C . Auger analysis also indicated the occurrence of Ag, Pd precipitates. Particles with a

1 similar Ag-Pd composition have been reported by Mausolf *et al.* [5]. Ray *et al.* [12] has also
2 examined oxide fuels with TEM and shown that the metallic particles ranged in size from 10 nm
3 to 0.5 μm . Evidence for the formation of fission product 4d metal nano-particles was also found
4 within the UO_2 matrix from the 2 billion year old Oklo natural reactor in the Gabon [13]. These
5 deposits are sufficiently ancient that all ^{99}Tc has decayed to ^{99}Ru . Utsunomiya and Ewing [13],
6 using TEM imaging demonstrated that the original epsilon metal particles were altered to
7 ruthenarsenite $[(\text{Ru},\text{Ni})\text{As}]$ from dissolution and re-precipitation.

8 Analysis of metal particles from corrosion tests on LWR used fuels, ATM-106 and ATM-103 by
9 Finn *et al.* [14] also described metallic particles on the nanometer size range. More recently, Cui
10 *et al.* [15] dissolved LWR fuel in H_3PO_4 and examined the metallic residue material. Using
11 TEM, the particles appeared to have a similar size range that indicated that the material was
12 relatively unchanged from the dissolution process. X-ray absorption spectroscopy (XAS) of this
13 residue confirmed that the solid was metallic and that Mo, Tc, and Ru all possessed coordination
14 environments consistent with metal-metal bonds.

15
16 The resistance of these 4d-metal particles to acid dissolution has been well known from fuel
17 reprocessing. Forsyth [16] and Kessinger and Thompson [17] reported during fuel dissolution
18 tests that a finely divided material remained after nitric acid digestion of a spent fuel. Similar
19 observations of metallic residue material derived from the acid digestion of spent fuel were
20 reported by Adachi *et al.* [18], where the amount of undissolved residue solids increased
21 disproportionately with burn-up. The only material identified with x-ray diffraction was the
22 hexagonal ϵ -(Mo, Tc, Ru, Rh, Pd) phase with composition 20Mo: 0.5-5Tc: 50-60Ru: 10Rh: 10
23 Pd. Wronkiewicz *et al.* [19] first suggested that the resistance of epsilon metal to water

corrosion suggested they might be useful as potential long-term waste forms for technetium. Fabricating a rhenium analog of the proposed technetium waste form was expected to require temperatures in the range of 2600°C [19–20]. To form the material, Wronkiewicz *et al.* [19] mixed and pressed high purity metal powders and electric arc-melted them in the presence of an argon-flushed atmosphere. More recently, Crum *et al.* [20] repeated this methodology and produced the 5-metal material. In their experiment, alloys of Ru-Re and Mo-Pd-Rh were re-melted together to produce the simulated 5-metal material. The TEM characterization of the metallic products produced by Crum *et al.* [20] is described in the supplementary section. The epsilon-ruthenium (ϵ -Ru) metal is a hexagonal close packed (*hcp*) structure with $P6_3/mmc$ space group and unit cell parameters $a = 0.271$ nm and $c = 0.428$ nm [6–8, 19, 20]. How this structure forms at the operational temperatures in the nuclear fuel is, at present, unclear.

Initial characterization of Approved Testing Material (ATM) -109, a spent fuel from a Boiling Water Reactor from the Quad Cities I reactor was performed by Wolf *et al.* [21] This fuel was in-reactor from February 1979 to September 1987, and again from November 1989 to September 1992. The original uranium oxide (UO₂) fuel was fabricated by the General Electric Company. The UO₂ fuels had an initial 3.0% ²³⁵U enrichment and an initial grain size of 30 μ m. The specimens had maximum a burn-up of 70.80 GWd/MTU. The spent fuel segments had been sent to PNNL for experimental applications following post-irradiation examination at Argonne National Laboratory [21–23]. The results of post-irradiation examination of the UO₂ fuel with Transmission Electron Microscopy at ANL are reported in the Supplementary section.

2. Experimental Section

2.1 Sampling

As of July 2013, the fuel had been cooling for approximately 21 years [21]. The fuel was extracted from its Zircaloy cladding by mechanical means. Because of the strong bond between the rim of the irradiated fuel and the zirconium sheath and Zircaloy cladding, it was likely that the extracted sample did not contain a significant amount of the cladding metals [24, 25]. Once removed from the cladding the material was crushed prior to any processing. The first sample, designated ‘sample ATM-109-Nitric’, was derived from ATM-109 dissolved in nitric acid. The second sample, designated ‘sample ATM-109-CP’, was derived from ATM-109 dissolved in an ammonium-carbonate and hydrogen-peroxide (termed carbonate-peroxide) solution developed by Soderquist and co-workers [24, 25]. Gamma spectra of each sample indicated the specific activity was approximately equal for both samples and confirmed the inclusion of trace amounts of radionuclides including as ^{60}Co , ^{134}Cs , ^{137}Cs , ^{154}Eu , ^{155}Eu , and ^{241}Am has been reported by Palomares *et al.* [26]]; however, they also reported mass concentrations for ^{99}Mo , ^{100}Mo , ^{100}Ru , ^{102}Ru , and ^{103}Rh from the same noble metal fraction examined in this study. These isotopes were not detectable during the EDS analysis, although, in the Supplementary section, we report supporting evidence for radioactive Cs and Sb from the TEM-EDS analysis.

2.2 Microanalysis with SEM and TEM

Analysis of spent nuclear fuels with TEM is a useful technique for providing microstructural information on the material, disposition of radionuclides, grain structures, and secondary phases [27-29]. Particles recovered from dissolved ATM-109 (aggregates that may have been up to a few microns in diameter) were slurried in water, placed in polyethylene vials. Sub-samples were

1 pipetted from these slurries onto carbon coated TEM copper-grids and standard carbon-tape
2 SEM mounts. The SEM examination was performed with an FEI (Hillsboro, OR, USA)
3 Quanta250™ field emission gun scanning electron microscope equipped with an EDAX (EDAX
4 Inc., Mahwah, NJ) compositional analysis system. Images were obtained under low-energy
5 secondary electron imaging conditions to reveal the surface morphology as clearly as possible.
6 The samples were examined with a FEI Tecnai™ T30 Transmission Electron Microscope (TEM)
7 operated at 300 keV. The TEM was equipped with an EDAX x-ray energy dispersive
8 spectrometer (EDS) and a Gatan Orius™ digital camera. Quantification of the TEM-EDS
9 analyses of the epsilon particles was performed using the high energy K-lines that are well
10 separated for peak fitting, were not significantly attenuated in the metallic nanoparticles, and
11 were in a low background portion of the spectrum. The magnification and camera lengths were
12 checked against a MAG*ICAL silicon standard. Diffraction patterns and electron micrographs
13 were analyzed with Gatan DigitalMicrograph™ 1.83.842 and custom scripts by Mitchell [30].
14 Simulated diffraction pattern were generated using CrystalMaker® 2.2, a crystal and molecular
15 structures program for Mac and Windows, and SingleCrystal®2.0.1, an electron diffraction
16 simulation program distributed by CrystalMaker Software Ltd., Oxford, England
17 (<http://www.crystallmaker.com>). Ring patterns were simulated using MS Excel.
18 Crystallographic Information Files (CIF) for 5-metal phases were obtained from the American
19 Mineralogist Crystal Structure Database (<http://rruff.geo.arizona.edu/AMS/>). Irradiation
20 simulations were produced using the SRIM-2008 code [31].

21 **3. Results**

22 Scanning electron microscopy (SEM) analysis of the ATM-109 specimens indicated that the
23 majority of the materials were 5-metal phase. The materials consisted of extremely small

particles that were agglomerated together. The overall agglomerate had a high surface area. Figure 1 shows scanning electron microscope image of residue material from the (A) carbonate-peroxide and (B) nitric acid dissolution of ATM-109 used fuel appeared to show a high surface area of the material. It was not possible to determine the surface area by other methods. There were no large readily observable differences in the morphology of the spent fuel that had gone through the acid digestion versus the carbonate-peroxide dissolution process when examined with SEM.

In Figure 2, TEM images of the metallic particle agglomerates and selected area electron diffraction (SAED) pattern from the nitric acid and carbonate-peroxide leached specimens are shown. The insert SAED patterns also show the expected ring pattern from *hcp* ϵ -Ru metal. The match between the ϵ -Ru phase and the experimentally obtained pattern from the collection of undissolved 5-metal material was extremely good. However, the SAED patterns consist of discrete reflections and a diffuse band. This suggests the occurrence of many small crystallites and an amorphous phase. The electron diffraction data from the strong reflections is also shown in Table 1 together with literature data from Cui *et al.* [12], Ellner [32], and Kleykamp [7,8]. The results from the two specimens conducted under different dissolution processes confirmed that the crystalline portion of the 5-metal solid possessed the ϵ -Ru *hcp* structure. For comparison, electron diffraction analyses of metallic particles in undissolved ATM-109 high burnup fuel are also listed in Table 1.

In Figure 3, high magnification images of epsilon particles demonstrated that it was composed of smaller particles on the order of a few nanometers across in a matrix of an amorphous material. Moiré fringes were clearly visible in (A) nitric acid dissolved ATM109 and (B) carbonate peroxide dissolved ATM109. The Moiré contrast is caused by misaligned overlapping crystals;

1 however, other areas show evidence for the formation of defect structures that may have resulted
2 from in-reactor radiation damage. The images indicate that many of the crystalline metallic
3 particles have particle diameters $<2\text{-}5$ nm. The amorphous material is most likely uniformly
4 spread throughout the particle. It is possible that the presence of amorphous regions resulted in
5 the rounded edges of the many of the epsilon particles. X-ray analysis of the particles was
6 conducted over numerous particles and these showed a slight variation in the Mo-Tc-Ru-Pd
7 content. It could be argued that the thickness variability and particle orientation may be
8 responsible for some of the observed differences; however, as ratio of the copper fluorescence
9 signal and the overall intensity of the weaker energy L-lines was invariant this indicates that
10 there was little attenuation of the x-ray signal from the K-lines of the $4d$ metals (Mo, Tc, Ru, Rh,
11 and Pd) and that the variability observed is real.

12 In Figure 4, the compositions of observed metallic particle compositions are plotted and
13 superimposed on the ternary phase diagram developed by Kleykamp [7, 8]. The variation in the
14 observed composition of undissolved fuel particles from ATM-109 indicated that these particles
15 may have been slightly affected by the dissolution process when compared to the compositions
16 of H_3PO_4 [15] and nitric acid [16-18] dissolved epsilon metal reported by others. However, there
17 was a difference between the acid digestion and the carbonate-peroxide process. There were
18 more ruthenium-rich phases found in the carbonate-peroxide dissolution process and a larger
19 range of smaller particles than found in the nitric acid dissolved processes. These results are
20 supported by the findings of Palomares et al. [26] who performed neutron activation analysis of
21 these extracted noble metal particles. Their results indicated that the nitric acid dissolved fuel
22 had a slightly lower Mo and Ru concentration than the carbonate-peroxide dissolved material.
23 This indicates that the two chemical processes may have had different effects on the metal

1 particles. It is also possible that these effects resulted in the formation of non-crystalline regions
2 in the metal particles.

3 The hexagonally packed ϵ -Ru structure is the lowest energy structure that would be expected to
4 form in the fuel. The occurrence of amorphous $4d$ metal clusters cannot be readily explained.
5 However, EDS analysis of the particles does indicate a small amount of uranium (see Figure 5).
6 There is a variation in the uranium content of the metal particles, and where the uranium is
7 present, the material looks less crystalline. The particles labeled 'c' and 'f,' possessed the highest
8 levels of uranium. This uranium content could be undissolved spent fuel that was not removed
9 during the dissolution processes. The uranium atoms would be incompatible with the ϵ -Ru
10 structure and the other $4d$ transition metals and may have induced an amorphous or 'frustrated'
11 metal structure to be retained. As the probe size of the TEM was larger than the nano-
12 amorphous regions within metallic particles, it was not possible to obtain definitive evidence on
13 the distribution of uranium in the metal and its connection with the amorphous regions. It is also
14 possible the amorphous regions could have been caused by chemical dissolution processes;
15 although, we would only expect such effects to be seen at the particle edges. Horlait et al. [33]
16 have shown using environmental SEM in-situ dissolution experiments that the triple points and
17 grain boundaries in mixed metal oxides corrode the fastest. As the noble metal phases in spent
18 fuels tend to form at triple points and grain boundaries, it is likely that they are released first
19 during the dissolution process.

20 When examining the intact fuel, the analyses tend to be biased toward the larger metallic
21 particles and there are fewer of these to examine. The extremely small metallic particles in the
22 fuel may have been missed during any normal post-irradiation examination. In Figure 6, a plot
23 of metallic particle volume for the two dissolution processes is shown. The mean particle size

was 43 and 58 nm, for the carbonate and nitric acid dissolution processes, respectively. This plot highlights the occurrence of exceedingly small nano-particles in the used nuclear fuels but is consistent with the studies by others [9, 15]. In a spent fuel dissolution study by Adachi *et al.*, [18] the average particle size of the undissolved residues from nitric acid were 68.4 nm after 2.5 hr of dissolution in 3M nitric acid and 117 nm after 3.5 hr. There was also an indication that the carbonate-peroxide dissolution process may have preserved these smaller particles; although, 1-2 nm diameter sized particles were also found in the nitric acid dissolved fuel. The preservation of the smaller particles supports the findings by Palomares *et al.* [26] of higher Mo, Ru, and Rh content in the peroxide-carbonate processed samples. However, although the particle size range appeared to be different, we would not necessarily expect a compositional difference, which was confirmed in the plot shown in Figure 4. These very fine particles combined with large particles with radiation-induced defects, may account for the reactivity observed in these phases observed by McNamara *et al.* [34].

Furthermore, the number of metallic particles available for analysis was small compared to the large number of different particles available from the nitric acid and carbonate-peroxide dissolved fuels.

4. Discussion

During nuclear reactor operation, the metallic particles in the uranium oxide fuel are distributed throughout the fuel matrix but have been observed principally at the grain boundaries and triple points [9, 10]. The process of dissolution of the fuel matrix has enabled us to examine these particles in greater quantity and more closely than previously and has enabled their structure to be revealed. The reactivity of epsilon metal particles will depend on their exposed surfaces.

1 Under accident scenarios, where the matrix is compromised, it is possible that these noble nano-
2 scale metal may act as catalysts as has been revealed in studies of Ag-Ru and Pd-Ru bimetallic
3 nanoparticles [35, 36]. McNamara and co-workers demonstrated that the specific epsilon
4 particles examined in this study exhibited significant exothermic vaporization with NF_3 [34].

5 The dissolution process is believed not to have resulted in changes to the surface of the metal
6 particles and the size range of the agglomerates was very consistent with the results of Cui *et al.*
7 [15]. However, their study was unable to probe the nanostructure of the individual metallic
8 particles and reveal the more complex structure. In this investigation, we have shown that the
9 individual particles of epsilon metal are highly faceted and have crystallite sizes on the order of
10 1-3 nm. This extremely small crystallite size may account for the high degree of reactivity
11 observed by McNamara et al. [34].

12 The limit on particle size range and the occurrence of amorphous (or ‘frustrated’) metal might be
13 a result of radiation damage during in-reactor operations combined with the introduction of low
14 levels of non-4d metals into the particles, particularly uranium. Meldrum et al. [37] and Lang et
15 al. [38] have investigated the formation nano-crystalline oxide phases under ion irradiation at
16 high temperatures in an effort to study the radiation induced thermal spikes that occur in these
17 materials. A similar process may be occurring within the 10-300 nm diameter ϵ -Ru phases
18 present in spent nuclear fuels that result in the generation of the complex nanostructure within
19 these particles. The sputtering of elements into the metal may lead to the generation of the
20 nanometer-sized particles and retention of the ‘frustrated’ amorphous structure. Frustrated metal
21 alloys are non-equilibrium structures that generally consist of nano-sized quasicrystals within a
22 specific compositional range. These alloys can be made by melt spinning methods or by
23 deformation methods and often possess high-ductility [39].

Using SRIM2008, a simulation of radiation damage was constructed from a high-energy fission fragments (900 keV Sr ions) similar SRIM simulations of irradiations by Hocking *et al.* [40] into an embedded epsilon phase in UO₂ (see Figure 7). The simulation consisted of a sandwich of UO₂ (5 µm) a helium gas phase gap (50 nm), and the 5-metal phase (200 nm). The helium gas gap was chosen to provide an artificial separation between the different materials in the simulation. There is no capability for running the SRIM code at realistic temperatures; however, the simulations can reveal important information regarding the pattern of damage in materials. At reactor temperatures, ~80% of the initial defects would be expected to self-anneal [40]. The results indicated that uranium could become embedded into the metallic phase and metallic elements would be sputtered into the UO₂. This hypothesis is supported by the experimental observations of extremely small metallic ε-Ru material and the detection by EDS of low levels of uranium in the metallic phase. However, the radiation damage simulation is limited as it does not account for temperature. What is required is a phase field simulation similar to that conducted by Li *et al.* [41] for fission gas bubbles in UO₂. Because of the significant, size difference between uranium metal ions and the 4d metals, the occurrence of uranium from radiation damage may the generation of an amorphous structure. This simulation may also explain why some uranium and plutonium was not removed during the chemical dissolution possibly because this material had become embedded into the metallic phase.

Higher resolution scanning TEM imaging with an aberration-corrected microscope [42, 43] that might be capable of resolving the compositional variation within the ε-Ru nanocrystallites might reveal the nature of the compositional differences and provide direct experimental proof why portions of the metal particles are amorphous. Furthermore, the amorphization of these metallic particles could be investigated in the future by using ion irradiation methods, similar to those

described by Meldrum *et al.* [37] and Lang *et al.* [38] to confirm if, fission fragments are responsible for localized amorphous regions in the metal. Lastly, the occurrence of actinides in the metallic particles, suggests that the concept of super-reprocessing, or complete isolation of the various radionuclides in spent fuel is not possible without complete dissolution of the ϵ -Ru metal phases. Recent nuclear waste disposal options have examined the potential for isolating undissolved material from spent fuel into a robust separate waste form [19-20]. Because the proposed waste form was considered to contain only the $4d$ metals, its disposal pathway would be more straightforward. However, this study indicates that the reason why dissolution processes have failed to completely remove actinides from the undissolved solids. It is because these heavy elements are trapped within the metallic particles and cannot be easily dissolved. Processing of such undissolved solid materials via high-temperature arc-melting for producing designer waste forms with specific radionuclide contents (i.e. waste forms containing only technetium) may not be a successful approach in the light of the discoveries presented here. There may always be a residual actinide content in the material derived from spent fuel.

5. Conclusion

By examining undissolved solids from used nuclear fuel, we have gathered new information regarding the nature of the ϵ -metal (epsilon phase) particles. The particles consisted of round particles between 10-300 nm in diameter, consistent with previous findings; however, the individual particles had not formed single crystals but owing to radiation damage had formed an extremely fine nano-structure consisting of distinct crystallites in an amorphous matrix. The electron diffraction patterns reflected this structure by producing diffraction spots and diffuse lines, indicative of an amorphous phase. Furthermore, discrete nanoparticles on the order of 1

1 nm in diameter were observed. It was not clear if these were amorphous or crystalline. Such
2 small particles residing in used nuclear fuels have not been reported previously. The major
3 elements in the metallic particles were Mo, Tc, Ru, Rh, and Pd; yet, the composition of these
4 particles varies a great deal. The smaller particles tended to be more ruthenium-rich and were
5 more prevalent in the carbonate-peroxide dissolved material which is in agreement with the
6 findings of Palomares et al. [26] who showed higher concentrations of Ru in the carbonate-
7 peroxide dissolved noble metal fraction compared to the nitric acid dissolved one. Previous
8 studies that had suggested single compositions or a very narrowly defined composition were
9 inaccurate in this regard. Minor amounts of other elements were also detected, including U. The
10 occurrence of detectable levels of actinides in these metallic residues suggests that they will not
11 be removed by conventional dissolution methods. Although the composition was variable, the
12 structure of the material was consistent with the hexagonal close packed structure of epsilon-
13 ruthenium. Similar phases can be formed synthetically from the separate metals only at
14 extremely high temperatures (i.e. $\sim 2200^{\circ}\text{C}$), whereas these phases form at relatively low reactor
15 operation temperatures. Actinides were found to have become embedded into the metallic
16 particle, which is probably due to radiation induced damage and deposition. Simulations with
17 SRIM appear to confirm this reasoning. The high reactivity of these solids observed by Cui et al.
18 [4] and McNamara et al. [34] might be explained by their exceptionally high surface area plus
19 the concentration of high-energy defect sites from radiation damage.

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Fig. 1. Scanning electron microscope image of residue material from the (A) carbonate-peroxide and (B) nitric acid dissolution of ATM-109 used fuel showing the exception high surface area of the material. The acid and carbonate-peroxide processes did not have a significant effect on the morphology of the undissolved solids but there were observed variations in composition.

Fig. 2. Bright field TEM image of metallic particle agglomerates from (A) Carbonate-peroxide dissolved (insert shows selected area electron diffraction (SAED) pattern and fit to ϵ -Ru *hcp* structure). The image in the bottom right hand corner is a higher magnification image of the epsilon metal particles clearly showing that some particles are isolated 1-2 nm particles and (B) Nitric acid dissolved ATM-109 used fuel with insert SAED pattern and match to ϵ -Ru metal.

Fig. 3A High magnification image of 20 nm diameter epsilon particle showing that it is composed of smaller particles on the order of a few nanometers across from carbonate peroxide dissolved ATM109.

Fig. 3B. High magnification image of particles from the nitric acid dissolved ATM109 solid.

Fig. 4 Plotted compositions of observed metallic particle compositions from the nitric acid and carbonate-peroxide dissolution processes, and from the received ATM-109 fuel. The data is superimposed on the Ternary plot developed by Kleykamp (1985).

Fig. 5 (a) TEM image of epsilon metal particles from nitric acid dissolution. **(b)** X-ray analysis of the particles showing a slight variation in the Mo-Tc-Ru-Pd content and the occurrence of uranium in some of the particles.

Fig. 6 Plotted cumulative distribution of volume of observed metallic particles from the two dissolution processes fitted to a log-normal distribution.

Fig. 7 SRIM calculation for 60 keV Sr fission product fragments passing through a hypothetical 5 μm UO_2 , 50 nm helium gap, and 3 μm thick particle of 5-metal phase, helium gap, and then UO_2 . The simulation shows U, Mo, and Ru atomic displacements and demonstrates that the radiation effects would be expected to result in significant re-distribution of metal.

Table 1. Electron diffraction analysis of metallic particles observed in ATM-109 high burn-up fuels

ATM-109-CP	ATM-109-Nitric	ϵ -Ru-(Tc,Mo,Rh,Pd)	β -Ru metal	Pd metal	Cui et al. (2012)
d_{obs} (nm)	d_{obs} (nm)	d_{lit} (nm) (hkl) ¹	d_{lit} (nm) (hkl) ²	d_{lit} (nm) (hkl) ³	d_{lit} (nm) (hkl) ⁴
	--	--	--	--	0.248, 0.249
0.238	--	0.2387 (010)	--	--	0.239, 0.238
0.232, 0.230	0.229	0.2210 (002)	--	0.2247 (111)	0.228, 0.224, 0.221, 0.218
0.214	--	0.2100 (011)	2.188	--	0.211, 0.209, 0.207,
0.199, 0.203	0.199	--	1.895	0.1946 (200)	0.199, 0.118, 0.205
0.165	--	0.1622 (012)	--	--	0.116
0.154	0.152	--	--	--	--
0.142, 0.136, 0.133	0.130	0.1378 (110)	0.1340	0.13764 (220)	--
0.121, 0.124	0.122	0.1254 (013)		--	--
0.117, 0.119	--	0.1193 (020)		0.11738 (311)	0.118
0.116	--	0.1169 (112)		--	0.116
0.114, 0.115	0.114	0.1152 (021)	0.1143	--	--
0.112	0.112	0.1105 (004)		0.11238 (222)	--
0.108, 0.106, 0.109	--	0.1050 (022)	0.1094		--
0.099, 0.100	0.101	0.1003 (014)		0.09723 (400)	--

¹ *hcp* metallic fission product phase ϵ -Ru(Tc,Mo,Rh,Pd) formed during irradiation ($\mathbf{a}$ = 0.276 nm, $\mathbf{c}$ = 0.443 nm) (Kleykamp et al., 1985).

² *fcc* ruthenium metal.

³ Pd metal (Fm3m) (Ellner, 1981) ($\mathbf{a}$ = 0.38930 nm).

⁴ d-spacings from TEM data taken from Cui et al. (2012) Table 2, pg 331.

Figure 1

Figure 2A

Figure 2B

Figure 3A

Figure 3B

Figure 4

Figure 5A

Figure 5B

Figure 6

Figure 7