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Literature review of thermal and radiation performance parameters for high-temperature, uranium dioxide fueled cermet materials

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Abstract

High-temperature fissile-fueled cermet literature was reviewed. Data are presented primarily for the W–UO_2 as this was the system most frequently studied; other reviewed systems include cermets with Mo, Re, or alloys as a matrix. Failure mechanisms for the cermets are typically degradation of mechanical integrity and loss of fuel. Mechanical failure can occur through stresses produced from dissimilar expansion coefficients, voids created from diffusion of dissimilar materials or formation of metal hydride and subsequent volume expansion. Fuel loss failure can occur by high temperature surface vaporization or by vaporization after loss of mechanical integrity. Techniques found to aid in retaining fuel include the use of coatings around UO_2 fuel particles, use of oxide stabilizers in the UO_2, minimizing grain sizes in the metal matrix, minimizing impurities, controlling the cermet sintering atmosphere, and cladding around the cermet.
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1. Introduction

Studies were conducted during the 1960s and into the early 1970s to develop fuel systems that could be used for a nuclear rocket reactor that would operate at temperatures up to 2500 °C. The materials in the fuel systems needed to be chemically and mechanically compatible with each other, as well as with the coolant/propellant, typically H_2. Thus, the materials needed to resist deterioration from H_2, as well as to withstand stresses introduced from thermal gradients.

Cermets, composed of a metal matrix with embedded ceramic particles were chosen as systems for study. Specifically, the cermet systems contained combinations of metals with a melting point greater than ~1325 °C and ceramics based on UO_2, UN, or UC. These materials were chosen because actinide ceramics are refractory and thermodynamically stable, and because the metal phase improves the composite's thermal conductivity and mechanical properties – principally ductility and toughness.

The most studied cermet has undoubtedly been the W–UO_2 system. Therefore, this cermet system is most frequently discussed in this report. Other cermet systems reviewed here include Mo–UO_2, Re–UO_2, W/Mo/Re alloys–UO_2. Uranium nitride

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fueled cermets were also studied, but are not reviewed here. The data reviewed here is inclusive of reports listed in the references, which are well representative, but not inclusive of all available data. Unfortunately, cermet reports are not easily accessible; this is for a number of reasons. Since the reports were typically written many decades ago, they are often in microfiche or paper format only. While theoretically available, there is not always a mechanism to obtain the reports from remote locations. Secondly, the reports are often contained in less available databases, including both databases closed to public parties as well as classified databases. Finally, many reports are classified, and while the information has been globally declassified, individual reports must proceed through a sometimes painful process for declassification.

The reports and papers reviewed for this report sometimes lack important details. Most notably, units are often not identified; during discussions for this report, unidentified units will be acknowledged. Readers are reminded that comparing data between different studies is difficult. Not only are units frequently missing, and both fabrication conditions and test conditions differing between studies, but the measurement conditions may also vary. For example, some researchers dissolved UO_2 from the surface of specimens before completing UO_2 loss experiments, while others did not. The varying surface treatments, not to mention varying specimen surface areas, would have a considerable effect on absolute UO_2 loss results. For this review, performance data is discussed in terms of significant experimental parameters along with information on sample composition and test details as appropriate and available. We attempt to show the effects of the important parameters on material properties and performance, rather than focusing on all absolute performance data.

The literature uses a variety of conventions to describe the composition of cermets. In this report, we have used a consistent nomenclature in which the metal component of the cermet is listed before an en-dash, which is followed by the ceramic component, i.e., a W–UO_2 cermet comprises UO_2 ceramic particles in a W metal matrix. Forward slashes separate the components of metal alloys, and parentheses isolate complex segments of cermet compositions. Therefore, the complex designation (W/30 at.% Re/30 at.% Mo-clad) W–60 vol.% UO_2 indicates a cermet with a W matrix filled with 60% UO_2 particles (by volume), and the entire cermet is clad by an alloy of W with 30 at.% Re and 30 at.% Mo. Also, the term *cladding* will refer to the material surrounding the fueled cermet core, and the term *coating* will refer to a thin layer around a ceramic particle. The term *fuel* refers to the fissile UO_2 material. In some cases, the cermet compositions given in the literature are not clear; we give the composition as our best interpretation of the authors intended meaning.

2. Cermet studies

Research programs on cermets containing fissile fuel were primarily carried out by several major laboratories, namely Argonne National Laboratory (ANL), General Electric Company (GE), Los Alamos Scientific Laboratory (LASL), Lewis Research Center (LRC), and Pacific Northwest Laboratory (PNL). The studies generally spanned the time period of the 1960s to early-1970s. The goals of the programs varied over time and between laboratories, but typically, cermets were envisioned to fission at temperatures exceeding 2000 °C for many hours, to withstand multiple thermal cycles, and to be operable in H_2 or inert gas coolants. During this decade plus of research, significant strides were made in understanding material issues and in improving performance of cermets. The reader should keep in mind therefore, that while failures were common during the development process, solutions were found for many of the challenges mentioned in this review. Later cermets were capable of repeated testing to extreme conditions without 'failure'. For example, a (W-clad) W–60 vol.% UO_2–10 mol% Gd_2O_3 cermets survived ~190 thermal cycles to 2500 °C in H_2 with only 1% (no unit) fuel loss [1]. Table 1 is a summary of issues, mechanisms, and solutions that were developed for UO_2-fueled cermets.

The LASL cermet program was directed toward production of refractory metal–UO_2 cermets for a nuclear propulsion reactor design. The operating temperature and environment were slated to be ~2300 °C in H_2. Results of the program appeared in reports that span the entire time period of cermet development, and include Lenz et al. [2], Lenz and Mundinger [3], Lenz [4], Lenz and Riley [5], and Riley and Taub [6]. LASL's early efforts were focused on detailed studies of UO_2-fueled cermets with a Mo matrix, including a study on radiation effects by Ranken and Reichelt [7]. Re–UO_2 cermets were also studied, with an eye toward improving

Table 1
Summary of performance issues, mechanisms, and solutions for high-temperature UO_2-fueled cermets

Issue	Mechanism	Solutions
Thermal performance		
Loss of mechanical integrity, leading to loss of UO_2 fuel	Formation of U at high temperatures that reacts to form uranium hydride with large volume expansion changes	Use of cladding that minimizes movement of species into or out of cermet structure
		Use of coating around UO_2 particles that minimizes UO_2 interparticle contact
		Use of oxide additives to UO_2, giving more chemical stability to the UO_2
		Sintering of cermet in a H_2O vapor environment to ensure complete O stoichiometry in UO_2
		Addition of additives (most notably ThO_2) to the metal matrix, which increase grain boundaries for storage of H_2 as well as path lengths for gas diffusion into the cermet. Additives also increase tensile strength and ductility
		Use of smaller metal matrix particles, which increase grain boundaries for storage of H_2 as well as path lengths for gas diffusion into the cermet.
		Fabrication of cermet with high theoretical density
	Formation of grain boundary phases that allow penetration of species into or out of cermet	Use of higher purity materials
		Cleaning treatments for materials, such as H_2 pretreatment and annealing
	Thermal expansion mismatch between UO_2, metal matrix, and cladding	Addition of additives (most notably ThO_2) to the metal matrix, which increase tensile strength and ductility
		Use of alloy for metal matrix that contains elements, such as Mo or Re (typically along with W), which enhance alloy ductility
Radiation performance		
Dimensional growth	Formation of solid products that are lower in density than surrounding material	Use of metal matrix with higher creep strength
	Formation of gas products with associated pressure	Lower density of cermet to allow space for gas fission products
		Use of interconnected porosity in cermet

performance through greater ductility. Later studies focused largely on W–UO_2 cermets and various cladding techniques. The program also delved deeply into metal ductility measurements and issues. Cermets were fabricated by cold pressing and sintering; powder rolling was also used for some cermets containing Mo in the matrix. Claddings were applied by various techniques including spray coating and gas deposition techniques.

ANL had a program to develop a fueled cermet for a nuclear rocket with associated extreme environment requirements. ANL studied W–UO_2 cermets, concentrating largely on fabrication techniques, including fabrication of complex shapes and development of a cladding process. Some physical property testing was also completed. The reports from this laboratory, specifically, Burt et al. [8] and Battles et al. [9], and ANL [1] are drawn from the mid-to-late-1960s. Samples were fabricated by either sintering of pressed compacts, isostatic pressing of compacts, or by pneumatic impaction of vapor-deposited-coated UO particles. Cermets were clad by vapor-deposition with W [1].

Work at PNL was presented in internal reports from the mid-1960s: deHalas et al. [10], Drumheller and Sump [11], Baker et al. [12], Nelson et al. [13], and Spanner and Brown [14]. The work was concerned with the development of a W–UO_2-fueled, H_2O-moderated space propulsion reactor. The program encompassed basic behavior and properties of

W–UO_2, W–UO_2 fuel fabrication studies, and other W–UO_2 fuel-development-related activities. Fabrication of the cermets was typically completed by a pneumatic impaction process; flow diagrams for processes using uncoated and coated UO_2 particles are given in Fig. 1(a) and (b) [12].

LRC completed studies on W–UO_2 cermets that could be used in a nuclear rocket system based on the use of an H_2O moderated reactor. H_2 was to be used as a propellant to maximize specific impulse. The LRC studies were all completed on W–UO_2 cermets. The studies include a well-rounded range of topics including fabrication development, fuel retention studies, and property evaluations. LRC discussed the results in reports that are almost entirely from the late 1960s, including Lietzke et al. [15] Saunders et al. [16], Ball and Sheibley [17], Sikora and Millunzi [18], and Blankenship [19]. Rolling processes for fabrication of cermets containing either uncoated or coated UO particles were developed. Both processes resulted in some elongation of UO particles, and therefore an iso-

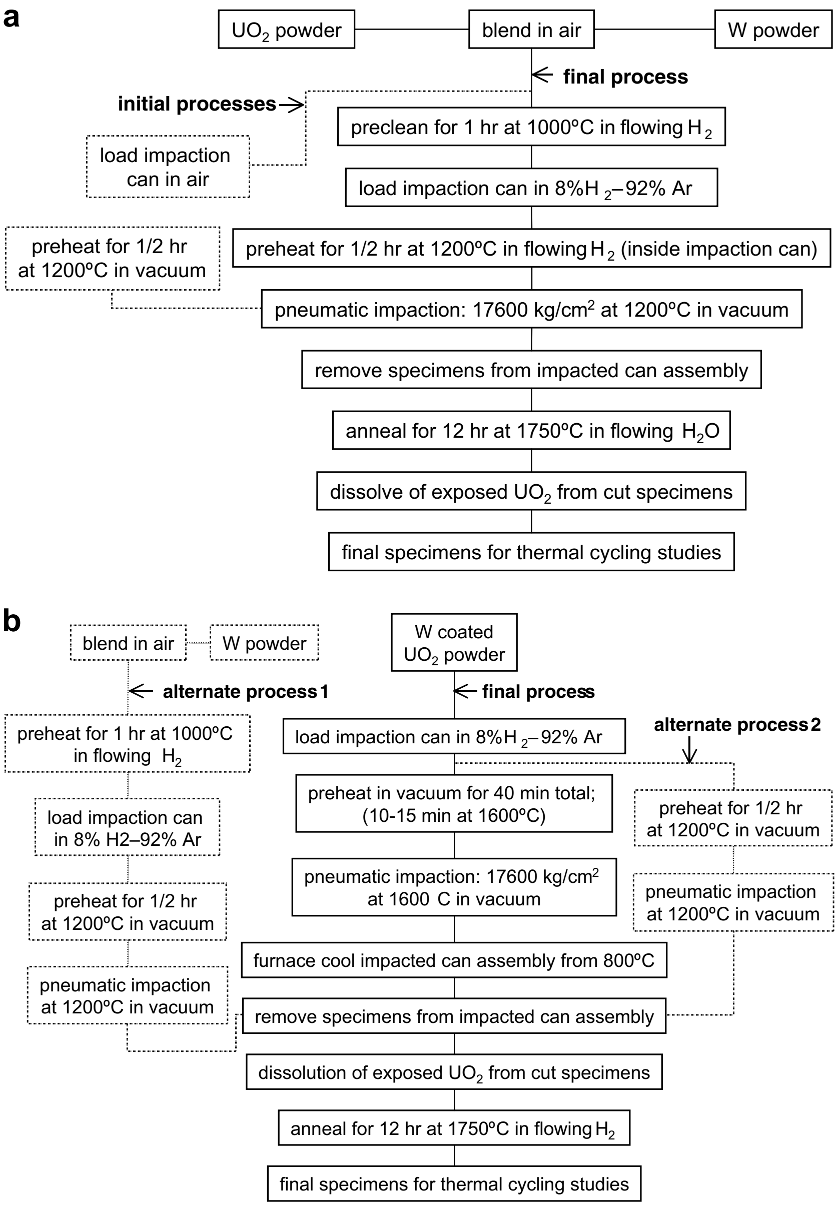

Fig. 1. Flow diagram of cermet fabrication processes at PNL using (a) UO_2 particles and (b) W-coated UO_2 particles.

static pressing technique was also used to a small extent; the isostatic pressing technique resulted in cermets of varying quality for LRC [1]. Flow diagrams for the rolling processes are given in Fig. 2(a) and (b).

GE Company's cermet program included extensive radiation testing of cermets; however, numerous experiments were completed using thermal testing alone. Thermal testing was generally completed at lower temperatures than for other programs. A number of different variables were tested, including use of W, Mo, and Re as metal matrices and various cladding compositions. This reviewed research is mostly from reports from the late 1960s, including reports by Collins and Newsom [20], Collins [21], Newsom and Collins [22], Newsom and Danforth [23], and a summary report [24]. Cermets were fabricated by pressing and sintering, followed by 'thermal cleaning' in wet H_2 and cladding by hot-gas pressure bonding. A flow diagram of the process is given in Fig. 3.

Some smaller programs on cermet research and development were present at other facilities. Hanford Engineering and Development Laboratory completed product development work, including thermal and irradiation tests of cermet fuel assemblies, as given in Carlson [25]. The Oak Ridge Gaseous Diffusion Plant completed studies on the fabrication of cermets by Foley et al. [26]. Further studies were conducted at this location, but they remain classified.

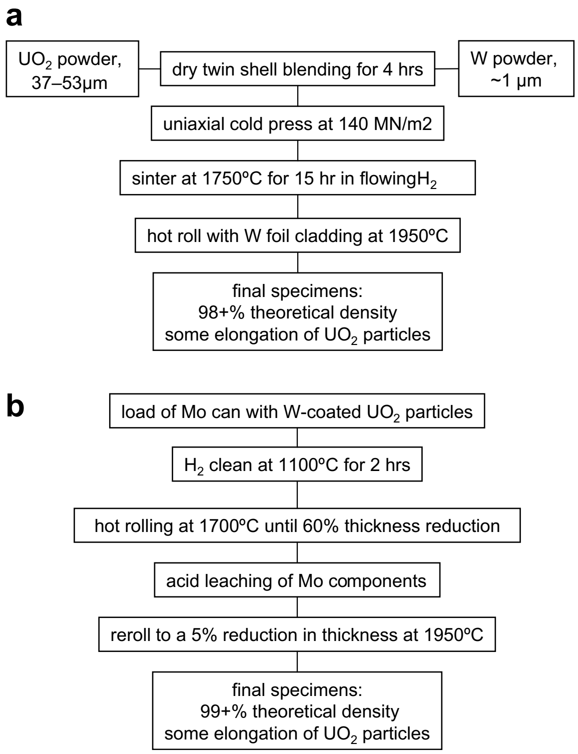

Fig. 2. Flow diagram of cermet fabrication processes at LRC using (a) UO_2 particles and (b) W-coated UO_2 particles.

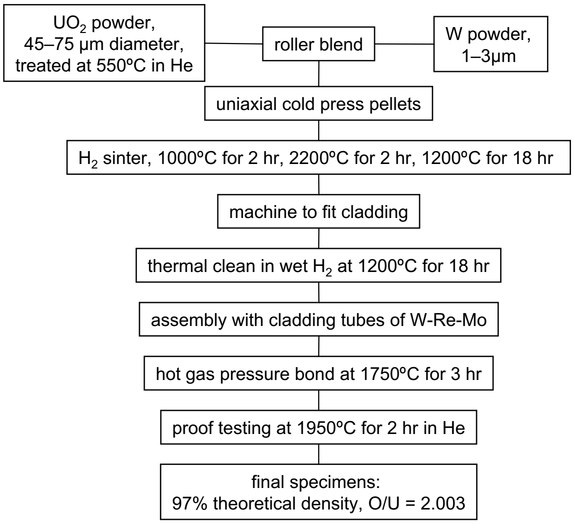

Fig. 3. Flow diagram of cermet fabrication processes at GE company.

3. Temperature performance

To measure cermet fuel and mechanical stability under controlled conditions similar to operation, thermal testing was often completed. Typically, specimens were repeatedly heated up to ~2000 °C within minutes and held at temperature for a span of approximately several minutes to an hour. Frequently, the samples were also cooled within minutes and cycled through the thermal process multiple times.

3.1. Thermal failure mechanisms

The failure modes for a cermet during operation of a nuclear rocket reactor are the loss of fissile fuel or the loss of mechanical integrity. The loss of fissile fuel, typically UO_2, may occur abruptly or gradually and is typically accompanied by a loss of mechanical integrity, either by complete disintegration or by lesser losses, such as cracking and blistering. The loss of mechanical integrity may also occur by separate mechanisms.

3.1.1. Fissile fuel loss

The mechanism for UO_2 fuel loss will depend upon where the fuel is located in the refractory metal matrix. Fuel that is located on the surface of a cermet is lost by high-temperature vaporization of UO_2, which has a vapor pressure of $\sim$400 N/m^2 at 2500 °C [16]. Fuel loss can also occur by diffusion through grain boundaries to the surface of the cermet. Losses are exacerbated by the interconnection of the UO_2 particles, microscopic pores and cracks in the refractory matrix, as well as by impurities, which can react or vaporize at high temperatures to cause defects in the fuel (e.g., C or F compounds). Vaporization loss is prominent when a specimen is held for long times at high temperatures [16].

For UO_2 located within the bulk of the cermet, a more complex mechanism for UO_2 loss is prevalent. When the cermet is heated to temperatures >1400 °C in an inert environment, UO_2 reduces to an oxygen deficient form and free oxygen, as shown in (1). As temperature subsequently decreases, the oxide returns to a stoichiometric state, leaving free uranium (2). Uranium and oxygen are then available in grain boundaries to migrate and react to form UO_2 again. Volume changes associated with these reactions disrupt the cermet and cause mechanical failure. A phase diagram of the uranium–oxygen system, shown in Fig. 4, illustrates these reactions.

$$UO_2 \rightarrow UO_{2-x} + xO \tag{1}$$

$$2UO_{2-x} \rightarrow (2-x)UO_2 + xU \tag{2}$$

When thermal cycling takes place in an H_2 environment, hydrogen penetrates into the cermet by bulk and grain boundary diffusion through the W matrix. The hydrogen combines with UO_2 fuel to produce an oxygen deficient UO_2, as seen in Eq. (3). Upon cooling, substoichiometric UO_2 disproportionates to free U and UO_2. Fig. 5 shows a micrograph of free U at grain boundaries in a thermally cycled W–20 vol.% UO_2 specimen. The free U, which has a melting point of $\sim$1130 °C, readily migrates along grain boundaries in the W matrix and rapidly forms UH_3 at $\sim$225 °C. The formation of UH_3 is accompanied by large increases in volume that can cause separation of W grains and create avenues for subsequent migration of UO_2 to the cermet surface. This migration results in loss of both UO_2 and mechanical integrity [16,8]. Fig. 6 shows the stages of fuel loss in an H_2 environment as a function of time.

$$UO_2 + H_2 \rightarrow UO_{2-x} + xH_2O \tag{3}$$

$$2UO_{2-x} \rightarrow (2-x)UO_2 + xU \tag{4}$$

Researchers confirmed the mechanism for bulk fuel loss at several laboratories [3,10,12], with further details added by additional researchers. For example, Baker et al. [12] stated that UO_2 migrates (as does H_2O) through grain boundaries to surfaces by formation of a W–UO_2 liquid. Saunders et al. [16] stated that free U not only forms UH_3 but also reoxidizes to form UO_2; both processes result in a large volume expansion, which can negatively impact mechanical integrity. Burt et al. [8] stated that the reaction to remove oxygen from UO_2 reaches equilibrium and does not proceed as long as path-

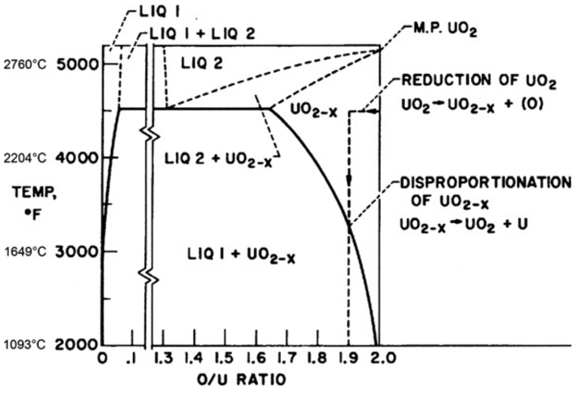

Fig. 4. Phase diagram of uranium–oxygen system showing changes in stoichiometry of UO_2 with temperature [15]. Celsius units have been added by the present authors.

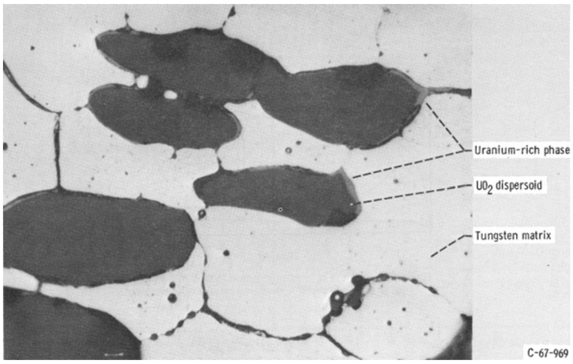

Fig. 5. Micrograph of thermally cycled W–20 vol.% UO_2 cermet showing free U at grain boundaries. The specimen was heat treated for five 1-h intervals at 2500 °C in H_2 with cooling to room temperatures between cycles [16].

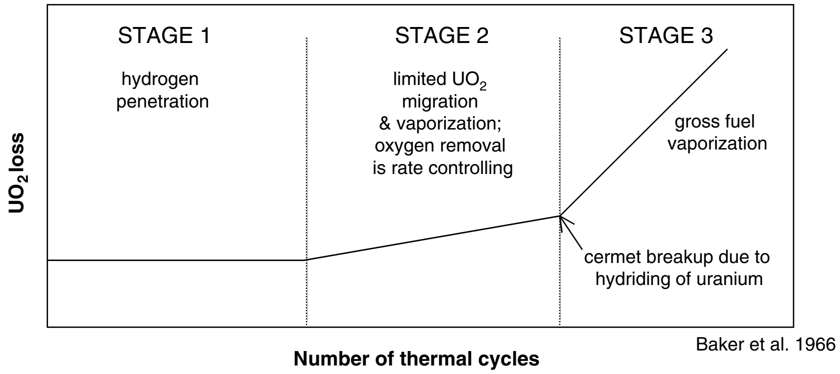

Fig. 6. Schematic showing the stages of UO_2 for cermets thermally treated in a H_2 atmosphere [12].

ways, such as a crack, are not present for removal of the product H_2O. Once a crack is present, however, the reaction proceeds.

3.1.2. Mechanical integrity loss

Loss of mechanical integrity is intimately related to fissile fuel loss, as described previously. However, there are further mechanisms for loss of mechanical integrity, most notably, vast differences in thermal expansion between the metal matrix and the ceramic particle. Repeated thermal excursions can lead to cracking and separation of the components in the cermet. Furthermore, irradiation (discussed later) can lead to swelling and changes in the cermet microstructure.

3.2. Experimental effects on thermal performance

Elucidation of the mechanisms of UO_2 fuel loss provided insight into experimental parameters and techniques that could be used for improving fuel loss performance. Results of experiments testing these insights are discussed in the following sections.

3.2.1. Test condition effects

3.2.1.1. Gas composition. Use of H_2 was compared with inert, vacuum, or oxidizing atmospheres during thermal cycling and was found to increase fuel loss. Saunders et al. [16] compared UO_2 loss results for W–20 vol.% UO_2 specimens thermally cycled to 2500 °C in H_2, He, or 0.5 Pa vacuum. The least UO_2 loss was seen for specimens cycled in He, which showed a linear loss rate with number of cycles, followed by specimens cycled in vacuum, and finally specimens cycled in H_2. The latter two groups both showed an initially linear UO_2 loss rate followed by a rapid increase in rate at a certain number of cycles. This rapid increase in rate is considered a point of catastrophic UO_2 loss, where structural integrity of the cermet is lost and the UO_2 loss rate is excessive. Two groups of researchers heated specimens in H_2 and then cooled them in He, isolating deleterious effects of H_2 to the cooling cycle. Lenz and Mundinger [3] noted the physical condition of specimens, (W-clad) W–50 vol.% UO_2 cermets, that were heated to 2600 °C and cooled in He or H_2. Specimens cooled in He were 'sound', while specimens cooled in H_2 were 'crazed'. deHalas et al. [10] completed thermal cycling experiments on W–13.3 vol.% (W-coated UO_2) specimens with either 4.14 MPa He or H_2 flowing at 16.5 L/min. The results show that while the initial UO_2 loss is greatest for the He-cycled specimens, after 15 cycles, the rate of UO_2 loss dramatically increases for the H_2-cycled specimens. deHalas et al. also studied the effect of thermal cycling to 2500 °C in 'wet' versus 'dry' H_2 environments. Thermal cycling W–20 vol.% (W-coated UO_2) cermets in dry H_2 resulted in much greater UO_2 loss than in wet H_2 after 15 cycles (~28%–no unit, as opposed to 4.1%–no unit). deHalas et al. [10] heated non-cermet specimens of UO_2 with 10 mol% ThO_2 or CaO at 2500 °C for 45 min in 4.14 MPa flowing H_2, followed by cooling in He or H_2. UO_2 cooled in He revealed only U inclusions in the microstructure, while UO_2 cooled in H_2 showed yellow-brown inclusions that were thought to be uranium hydride.

Baker et al. [12] completed experiments in which W bicrystals were placed over UO_2 fragments, in order to determine the effect of UO_2 vapor and to study W–W grain boundaries. Specimens that were thermally cycled to 2500 °C in 4.14 MPa He with a flow of 16.5 L/min showed far less void formation at the grain boundaries than specimens cycled in

0.101 MPa H_2. H_2 was deemed to accelerate UO_2 decomposition by lowering oxygen partial pressure and by contributing to grain boundary void and fracture effects [10,12,16]. deHalas et al. [10] also speculated that UO_2 decomposition may be greater in H_2, as compared with He, as a result of differing high temperature rheological properties between H_2 and He

3.2.1.2. Gas pressure. Increasing H_2 gas pressure during thermal cycling increased UO_2 loss for W–UO_2 cermets. Saunders et al. [16] measured UO_2 loss for (W-clad) W–35 vol.% (UO_2 with 10 mol% Ce_2O_3) cermets thermally cycled to 2500 °C in 0.101 MPa or 4.14 MPa (1–40.8 atm) H_2. At 25 thermal cycles, there was no UO_2 loss difference between the specimens; at 50 cycles, the 4.14 MPa cycled specimen showed approximately ~1.5 wt% greater UO_2. deHalas et al. [10] showed more dramatic disparities for W–20 vol.% UO_2 specimens thermally cycled to 2500 °C in either 0.101 MPa or 4.14 MPa H_2. After 25 cycles, the specimens cycled at the higher pressure showed ~12% (no unit) to infinitely more UO_2 loss, dependent upon the gas flow rate. Further measurements were completed for W–9.4–20 vol.% UO_2 cermets (with and without W coating on the UO_2 particles) that were thermally cycled to 2500 °C in H_2 pressures ranging from 1.38 to 6.89 MPa, and with both static and 16.5 L/min H_2. The same trend of increased UO_2 loss with increased H_2 pressure was observed by Baker et al. [12], although the degree of disparity between results from the two pressure regimes depended on experimental conditions. Baker et al. indicated that visual examination of specimens cycled at higher H_2 pressure qualitatively showed a greater presence of surface microcracks.

Experiments on W bi-crystals in the presence of UO_2 fragments, which were thermally cycled to 2500 °C in either 0.101 MPa or in 4.14 MPa H_2 with a flow of 16.5 L/min, resulted in catastrophic fracture at the grain boundary for the bi-crystals treated in 4.14 MPa H_2. The bi-crystal treated in 0.101 MPa H_2 did not fracture, but resulted in large grain boundary 'bubbles'. The effects of increased H_2 pressure were considered to be a result of an enhanced drive for hydrogen diffusion into the cermet at greater H_2 pressures, as well as an increased absolute content of H_2 [12].

In addition to demonstrating a directly proportional effect between UO_2 loss and test gas pressure, Baker et al. also showed a reverse H_2 pressure effect for some W–(W-coated UO_2) cermets. W–41.3 vol.% (W-coated UO_2) and W–29.8 vol.% (W-coated UO_2 with 10 mol% Y_2O_3) specimens, which were thermally cycled to 2500 °C in 0.101 MPa or 4.14 MPa H_2 with a flow of 16.5 L/min, showed less UO_2 loss at 4.14 MPa H_2 than analogous specimens cycled at 0.101 MPa H_2. The latter cermet showed a wide spread in the data with a crossover point at ~40 cycles where subsequent cycling resulted in greater losses at higher pressure H_2. Authors claimed that the crossover point corresponded to the point of complete removal of UO_2 on the outer surface of the cermet. Microscopic examination revealed that UO_2 loss was primarily from outer layers of the cermets, and therefore the authors felt that the reverse pressure phenomena might have been related to surface fabrication effects for non-clad cermets [12] (specimens contained 44–53 μm UO_2 particle diameter with a 10 μm W coating, 98.7% theoretical density–TD). deHalas et al. also saw the reverse pressure effect for W–35 vol.% (W-coated UO_2) cermets subjected to the same thermal cycling conditions as described for Baker et al. [10].

3.2.1.3. Gas flow rate. Increasing the flow rate of gas greatly increased UO_2 loss. A (W-clad) W–13.3 vol.% UO_2 cermet lost 1.9% UO_2 (no unit) during 25 thermal cycles to 2500 °C in 4.14 MPa static H_2, while a nominally identical sample lost 50.2% UO_2 (no unit) and deteriorated to powder during testing in 4.14 MPa H_2 flowing at 16.5 L/min. The rate of UO_2 loss becomes catastrophic at a lower number of thermal cycles for the specimens treated in the flowing H_2 environment [10]. Other studies on W–UO_2 cermets showed similar results [10,12]. Researchers concluded that flowing gas accelerates UO_2 loss by removing gaseous products, thus maximizing the concentration gradient drive for reactions to continue. The accumulation of gaseous products suppresses further reaction, thus preventing further UO_2 loss [10,16].

3.2.1.4. Temperature. Several researchers observed a greater fuel loss for W–UO_2 specimens thermally cycled at higher test temperatures. The degree of disparity between test temperatures depended not only on the temperatures used, but also on the specimen composition. Saunders et al. [16] measured the effect of maximum temperature during thermal cycling on UO_2 loss for (W-clad) W–25 vol.% (UO_2 with 10 mol% Ce_2O_3) specimens cycled in flowing H_2. After 25 cycles, the specimen cycled at 2500 °C showed ~1 wt% loss, while the specimen cycled at 2600 °C shows ~1.5 wt% loss. Catastrophic UO_2 loss began at ~100 thermal cycles for the 2500 °C cycled specimen and at ~20 cycles for the 2600 °C cycled specimen; therefore, the disparity between the specimens became much greater with increased numbers of thermal cycles. Baker et al. [12] observed a ~3 wt% difference after ~15 cycles between W–13.3 vol.% (W-coated UO_2) thermally cycled at 2350 °C or at 2500 °C. Data for the same cermet materials were tested with accelerated test conditions of 6.89 MPa H_2 and 2450–2600 °C. The trend of greater UO_2 loss with increased temperature was observed, but the data at 2600 °C had large deviation. deHalas et al. [10] observed ~2% UO_2 (no unit) loss at 2150 °C as compared with ~30% UO_2 (no unit) after 15 cycles to 2500 °C in dry H_2 for W–20 vol.% (W-coated UO_2) specimens.

Mo–UO_2 cermets also show an increased UO_2 loss with increased test temperature. Lenz et al. [2] determined UO_2 losses for Mo–20 vol.% UO_2 specimens held at elevated temperatures in flowing H_2 or vacuum for various amounts of time. For a 10-min hold at maximum temperature, a sudden increase in UO_2 loss occurs when temperatures exceed ~2500 °C. The temperature region at which UO_2 losses begin to significantly increase corresponds to the temperature at which UO_2 vaporization begins.

3.2.1.5. Time at temperature. Experiments to test the effects of time at temperature showed that longer times at maximum temperature increased total fuel loss. Saunders et al. [16] showed the effect of time at temperature for unclad and partially clad W–20 vol.% UO_2 specimens. After an initial rise in UO_2 loss, the rates of fuel loss were linear. Lenz et al. [2] showed the effect of heating time for up to 30 min on UO_2 losses in Mo–20% (no unit) UO_2 cermets. UO_2 loss initially increased quickly with heating time, followed by a linear increase. The linear rate depended upon the conditions of the test as well as the fabrication parameters of the cermet. UO_2 losses from 10 min at 2550 °C were ~3 times the losses from 10 min at 2280 °C.

3.2.1.6. Isothermal and cyclic heating. Cermets that received thermal cycling, rather than isothermal heating, showed greater UO_2 loss for the same amount of time at temperature. deHalas et al. [10] demonstrated that W–20 vol.% (W-coated UO_2) cermets either thermally cycled or held at 2500 °C in H_2, lose UO_2 at a greater rate for the former case. Three hours at 2500 °C (or 15 cycles) resulted in a ~10 times increase in UO_2 loss between cycled and isothermally treated specimens. A similar, but somewhat different trend, was seen for W–20 vol.% UO_2 cermets treated at 2500 °C in H_2. UO_2 loss after isothermal and thermal cyclic testing is the same up to a point of catastrophic UO_2 loss in the cycled specimen, where the UO_2 loss rate dramatically increases. This behavior is also seen for (W/30 at.% Mo/varying additions Re)–40 vol.% UO_2 cermets with claddings thermally cycled to 2600 °C in He. Specimens that were cycled in 5-min cycles showed catastrophic UO_2 loss at much less time than specimens cycled in 30-min cycles. Increasing numbers of thermal cycles also caused specimen geometric growth [4]. Results showed a reasonably linear relationship between diametral growth and number of thermal cycles, for a variety of W and Mo based UO_2 cermets [20].

3.2.1.7. Heating and cooling rates. Saunders et al. [16] concluded that heating and cooling rates during thermal cycling had a small effect on UO_2 loss for the ranges studied. Saunders et al. measured UO_2 loss for W–20 vol.% UO_2 specimens with heating/cooling times to 2500 °C of either 10 min or 15 s. After 10 cycles, the less quickly heated/cooled specimen showed ~10 wt% more UO_2 loss; however, both specimens reached catastrophic UO_2 loss at the same number of thermal cycles and lost UO_2 at a fast rate by 10 thermal cycles. Lenz [4] showed that (W/30 at.% Mo/varying additions of Re)–40 vol.% UO_2 specimens and (W/25 at.% Re)–40 vol.% UO_2 specimens with various claddings thermally cycled to 2600 °C in flowing H_2 resulted in UO_2 loss at lesser number of thermal cycles when a shorter thermal cycling time was used.

Baker et al. [12] observed different results: sample integrity improved with a slower heating rate during thermal cycling (grain boundary voids were still present). In experiments on W crystals, which showed grain boundary rupture (at large grain boundary misorientation), the failure always occurred explosively and during heating. The experiments suggested a mechanism for the effect of heating and cooling rates on UO_2 loss in H_2. During heating, monatomic H forms on W surfaces and penetrates W grains (according to the solubility of H in W). During cooling, H exsolves from the W and recombines at W grain boundaries. When cooling is sufficiently rapid, H is trapped at the W grain boundaries and during subsequent heating provides pressure that ultimately causes grain boundary rupture.

3.2.2. Fabrication condition effects

The major techniques found in the literature that were used to fabricate cermets include uniaxial pressing and sintering, roll compaction, hot isostatic pressing, hot pneumatic impaction, green state forming and sintering, hot extrusion, vapor cementation, magnetic pulse forming, and high-pressure preslugging. Vapor cementation and magnetic pulse forming were not developed enough to produce a cermet with all the attributes that were desired by researchers completing the studies. Roll compaction and hot extrusion produced cermets with elongated grains, which introduced texture and anisotropic properties; although anisotropy or texture were not desired in all cases, they can be advantageous. Green state forming and sintering, hot isostatic pressing, and hot pneumatic impaction all allowed graded fuel loadings and production of complex configurations (honeycomb grids) [16]. High-pressure preslugging was not described, but it was reported to result in a high level of interconnected porosity [25]. Many of the techniques also required a sintering or annealing step to produce the final product.

3.2.2.1. UO_2 fuel loading. Mixed results have been obtained for the effect of increased UO_2 loadings in cermets on the percentage of UO_2 loss during thermal treatment. Baker et al. [12] determined that increased loading of UO_2 reduced the percentage of UO_2 loss for W–UO_2 cermets, with and without W coating on the UO_2 particles, when thermally cycled to 2500 °C in 4.14 MPa H_2 flowing at 16.5 L/min. For a test with W–(W-coated UO_2) cermet, the specimen with a 13.3 vol.% UO_2 content exhibited catastrophic UO_2 loss at fewer thermal cycles than its 32.3 vol.% UO_2 counterpart, but upon onset of catastrophic failure, the rates of UO_2 loss were reported to be similar. Baker et al. noted further, that the absolute mass of UO_2 lost for specimens of various loadings was similar and, therefore, suggested that a product removal step may be the rate-controlling step for UO_2 loss.

An effect of UO_2 loading was also demonstrated by Saunders et al. [16] for W–UO_2 cermets with 10–35 vol.% UO_2 that were thermally cycled to 2500 °C in flowing H_2. Specimens with increased UO_2 loading clearly show earlier onset of UO_2 loss with subsequent UO_2 loss rates appearing similar. This result opposes the results obtained by Baker et al. [12]; it may be that the relationship between UO_2 loading and UO_2 loss is more dependent on specimen variables such as surface area or density, than fuel loading.

3.2.2.2. UO_2 fuel oxygen stabilizers. Various oxides, including ThO_2, ZrO_2, CaO, Dy_2O_3, Eu_2O_3, Gd_2O_3, Sm_2O_3, Y_2O_3, and Ce_2O_3, form face-centered-cubic solid solutions with UO_2 at 5–10 mol% levels [8]. Several of these oxides, as well as others, were tested with UO_2 fuel for their oxygen stabilizing ability during thermal testing. The presence of most oxide additions significantly decreased UO_2 losses.

Fuel loss tests for face clad W–35 vol.% UO_2 cermets with 10 mol% additions of 13 various oxides or combinations of oxides to the UO_2 were tested. A range of improvements to UO_2 loss was obtained, with some oxides dramatically decreasing loss from >95 wt% to ~10 wt% after 20 cycles to 2500 °C in flowing H_2. Y_2O_3 and Ce_2O_3 were chosen for further study. UO_2 losses with either additive were very similar, with Ce_2O_3 additive showing slightly (<1 wt%) better performance after 100 cycles as compared with Y_2O_3 and a microstructure with less UO_2 migration. Additions of Ce_2O_3 (2.5–10 mol%) during thermal cycling to 2500 °C in flowing H_2 were studied; the larger addition clearly resulted in the least amount of UO_2 loss [16]. deHalas et al. conducted experiments using W–20 vol.% UO_2 in which 0.27 wt% CaO was added to the UO_2 and 1.20 wt% ThO_2 was added to the W matrix (see later discussion for effects of ThO_2 in the metal matrix). After thermal cycling to 2500 °C in flowing 4.14 MPa H_2, specimens with CaO and ThO_2 additions showed 28% (no unit) UO_2 loss while analogous non-modified specimens showed >30% (no unit) loss [10]. In experiments by Burt et al. [8] of various W–UO_2 cermets thermally cycled to 2450 °C and 2500 °C, the top performing cermet was a Gd_2O_3 stabilized cermet, specifically (W-clad) (W–36.2 wt% UO_2–2.7% Gd_2O_3). It showed gradual UO_2 loss after 60 cycles. Lenz measured UO_2 loss for (W/30 at.% Mo/varying additions of Re)–40 vol.% UO_2 cermets with and without additions of 4 vol.% Y_2O_3 to the fuel, which were thermally cycled to 2600 °C. Y_2O_3 stabilized cermet clearly showed the least amount of UO_2 loss, ~0.5% (no unit) for the stabilized cermet as compared with essentially infinite loss for the non-stabilized cermet after several thermal cycles [4]. Thermal cycling of specimens of fuel only, specifically UO_2 with and without UO_2–CaO, showed appreciably more precipitated U in UO_2 as compared with UO_2–CaO [10].

Phase boundary studies of oxides added to UO_2 revealed that oxide additives have no significant effect on the position of the solvus curve representing the separation of U from UO_{2-x}. Therefore, oxide additives do not increase the solubility of U in UO_2 but must stabilize UO_2 against loss of oxygen [16]. deHalas et al. postulated two mechanisms for the stabilizing effect of oxide additions to UO_2: (1) an oxide additive lowers the partial molar free energy of oxygen in the ceramic phase without the possibility of forming free metal on cooling and (2) with the addition of oxide, U is transformed to the hexavalent state, which does not reduce to U metal. UO_2 will maintain an oxygen-to-metal ratio of 2.0 to 2.1 with additions of rare earth oxides by forming a defect lattice structure. To maintain electrical neutrality, some U atoms are in the hexavalent state; U^{4+} cannot be reduced to metal in the presence of U^{6+}, therefore, initial loss of oxygen from cermets is accompanied by creation of anion vacancies rather than formation of U metal. The UO_2 remains intact until all U^{6+} atoms are reduced at which point formation of U metal (and subsequent hydriding) will no longer be inhibited [10].

3.2.2.3. UO_2 fuel O to U ratio. Baker et al. [12] completed a study of W–20 vol.% UO_2 cermets in which the O/U ratio of the starting composition was varied from 1.93 to 2.05. The ratio was determined to have only a minor effect on the UO_2 loss behavior of cermets thermally cycled to 2600 °C in 6.89 MPa static H_2. The researchers suggested that a change of O/U to 2.00 may have occurred in the cermets during fabrication. This result, regarding starting compositions, should be distinguished from results in which cermets change stoichiometry during operation, which can alter performance characteristics.

3.2.2.4. UO_2 fuel particle size. Mixed results were obtained for the effect of UO_2 particle size on UO_2 loss during thermal testing. It may be that this parameter has a complex relationship with other parameters or may not easily be isolated. For example, processing to form different particle sizes could incur unexpected variations, such as contamination, that confuse results. Also, product resulting from different particle sizes could add variations, such as different sintered densities.

A study by Saunders clearly showed that cermets containing small UO_2 particles lose less UO_2 fuel when heated as compared with cermets containing larger UO_2 particles. Saunders et al. [16] compared performance for W-face-clad 20 vol.% UO_2 cermets containing ∼50-μm and ∼1-μm particles of UO_2 that were thermally cycled to 2500 °C in H_2. The smaller particle size material showed significantly improved UO_2 retention, but the high-temperature tensile strength was found to decrease with smaller UO_2 particle size. No explanation was given for the improved fuel retention capability. Comparisons of UO_2 losses by Baker et al. [12] from W–20 vol.% UO_2 cermets containing either micronized <4-μm diameter UO_2 or arc-fused 44-μm diameter UO_2 thermally cycled to 2600 °C in 6.89 MPa static H_2 show that cermets with the smaller sized UO_2 tend to have lower UO_2 losses after 10 thermal cycles.

Directly opposite UO_2 loss results for cermets made from co-precipitated mixtures of W and UO_2 were obtained by Baker et al. [12]. Unfortunately, no indication of particle size is given for coprecipitated powders, but it is likely that the powders are finer than other powders used in the study. The authors stated, however, that the appearance of the coprecipitated powders indicated probable impurity contamination. Burt et al. [8] also showed results in which cermets containing coarser particles gave better UO_2 loss performance; under thermal cycling at 2460 °C in H_2, W–50 vol.% UO_2 that contained 'micronized' (smaller) UO_2 particle sizes failed more quickly than a cermet containing 'ceramic grade' (larger) particle sizes. No explanation was given for the particle-size effect.

Lenz et al. [2] completed a more thorough study of Mo–20% (no unit) UO_2 cermets with different UO_2 particle sizes. He determined that thick specimens (low surface to volume ratio) lost greater percentages of UO_2 when the cermet contained smaller UO_2 particles (2.3 μm versus 4.4 μm diameter), while thin specimens (high surface to volume ratio) lost greater percentages of UO_2 when the cermet contained larger UO_2 particles (4.4 μm diameter). The particles also differed in density, with the smaller UO_2 particles having a lower density. Based on studies of Mo–UO_2 cermets and a belief that UO_2 losses from a metal matrix proceed by evaporation through fissures or by grain boundary diffusion, Lenz et al. theorized that cermets with a metal phase below theoretical density should exhibit decreasing UO_2 losses as the diameter of UO_2 particles increases because of the decreasing surface-to-volume ratio as particle size increases.

3.2.2.5. UO_2 Fuel particle coatings. In some studies, UO_2 particles were coated with W before being combined with refractory metal particles to fabricate a cermet. UO_2 loss performance results were favorable for the W coating of UO_2 particles. Saunders et al. [16] reported that unclad W–20 vol.% UO_2 cermets resulted in ~23 wt% UO_2 loss when tested at 2500 °C for 2 h in H_2, whereas the same material with W–coated UO_2 particles resulted in ~0.80 wt% loss. deHalas et al. [10] also determined that coating UO_2 particles with W in unclad W–UO_2 cermets improved fuel retention. For clad cermets, the same trend was observed (although to a lesser degree): ~0.20 wt% loss for fully clad W–20 vol.% UO_2 cermet versus ~0.15 wt% loss for an analogous cermet with non-coated particles. deHalas et al. [10] measured UO_2 loss of a W–(13.3 vol.% W-coated UO_2) cermet with a thick W particle coating (16 μm rather than 4.5 or 10 μm) after thermal cycling to 2500 °C in 16.5 L/min H_2 at 4.14 MPa. The specimen performed well in comparison to all other specimens, particularly at low numbers of thermal cycles. Saunders et al. [16] recommended the use of W-coatings on UO_2 particles, preferably applied by hydrogen reduction of WCl_6, as well as adding ThO_2 to the W coating, to improve fuel retention and increase strength. Coating UO_2 particles prevents particle interconnection and presumably slows the deleterious reactions between UO_2 and H_2 that occur during thermal cycling. Coating particles is similar to effects of cermet claddings. This result is particularly true for unclad cermets that contain exposed UO_2 on surfaces [16]. Particle coatings also result in a more uniform and continuous W matrix, a uniform fuel distribution, and complete separation of the UO_2 particles [18]. deHalas et al. [10] also concluded that coated UO_2 particles give greater grain boundary strength to the W matrix, which thereby minimizes fuel loss. Electron microscopy of a 2500 °C thermally cycled specimen containing W–13.3 vol.% (W-coated UO_2) revealed reaction layers between particles and their coatings. Baker et al. [12] speculated that the reaction layers were the result of halide impurities at the coating/particle interface, a W–UO_2 eutectic interaction, or the formation of W–U–O ternary compounds.

Burt et al. [8] obtained a different result (greater fuel loss) as the effect of W coating on UO_2 particles for a W–25 vol.% UO_2 cermet. The researchers believed that the increased UO_2 loss with W coating on UO_2 was a result of fracture caused by thermal expansion mismatch between UO_2 and the W coating. It should also be noted, however, that the specimen containing the W-coated UO_2 particles was made by a different fabrication procedure than other specimens in the study. The particles were 'Dynapak consolidated' at 1200 °C, a temperature considerably below the typical sintering temperature of other cermet specimens, approximately 2400 °C, and below the pneumatic impaction temperature of 1600 °C used by deHalas et al. [10] and Baker et al. [12]. The Dynapak process is a high-strain rate powder pressing process, which is probably similar to pneumatic impaction. Collins [21] reported unfavorable results for the use of chemical-vapor-deposited W on UO_2 particles after thermal cycling of a (W/30 at.% Re/30 at.% Mo clad) W–60 vol.% UO_2 cermet. The diametral growth of specimens was more than twice that of cermets with uncoated UO_2. The authors did not examine the microstructure of the coated particle cermet, but assumed that the large growth was due to a loss of mechanical integrity in the W matrix.

3.2.2.6. Metal matrix additives. ThO_2 was added to the W matrix in studies to reduce UO_2 fuel loss. Saunders et al. [16] demonstrated the effect of 2 vol.% ThO_2 added to the matrix of W–20 vol.% UO_2 cermets and thermally cycled to 2500 °C in H_2. The specimens with ThO_2 additions show reduced UO_2 losses as compared with non-ThO_2 counterparts. Baker et al. [12] compared UO_2 loss performance of two W–20 vol.% UO_2 cermets, with one having a 1.20 wt% addition of ThO_2 to the matrix. Thermal cycling to 2500 °C in static H_2 showed equivalent UO_2 losses for the two cermets, but cycling in 16.5 L/min H_2 resulted in lower UO_2 losses from the cermet with a ThO_2 addition after 10 cycles. Added ThO_2 resulted in dispersed phases in the W microstructure that inhibited grain growth and produced two effects that were favorable to UO_2 loss: (1) more grain boundaries were available to store hydrogen, and (2) the path length for hydrogen diffusion into the cermet was increased [12]. The addition of 2 and 6 vol.% ThO_2 into the metal matrix of W–UO_2 cermets also improved the tensile strength of the cermet [16] and its ductility after heating [4]. The cause of these improvements was not determined. Lenz [4] conducted experiments in which 4 vol.% Y_2O_3 was added to the metal matrix of (W/30 at.% Mo/12 or 17 at.% Re)–40 vol.% UO_2 and thermally cycled to 2600 °C in flowing H_2. UO_2 losses decreased when Y_2O_3 was added to the metal matrix. The decreases in losses were not as notable, however, as when Y_2O_3 was added to the UO_2. Y_2O_3 was also noted to improve the ductility of cermets. ThO_2 and Y_2O_3 were tested as an additive for both the matrix and oxide fuel; the reader should be careful to distinguish between the different effects of these oxides when it is added to the matrix or incorporated in the fuel particles.

3.2.2.7. Metal matrix particle and grain characteristics. Another way to reduce fuel loss during thermal cycling is to use smaller W particles when fabricating W–UO_2 cermets. The concept is similar to the use of ThO_2 in the metal matrix, where resulting cermet microstructures have decreased grain sizes and an increased number of grain boundaries for storing hydrogen. Comparison of W–24 vol.% (W-coated UO_2) cermets thermally cycled to 2500 °C in 4.14 MPa H_2 at 16.5 L/min showed that UO_2 losses were lower for the specimen that was fabricated with additions of 1-μm-diameter W as opposed to the specimen fabricated with 5-μm-diameter W.

Baker et al. [12] studied the effect of grain boundary mismatch (difference in grain orientation at grain boundary) on W bi-crystals adjacent to a plug of UO_2 and subjected to thermal cycling to 2500 °C at 4.14 MPa H_2 and at 16.5 L/min. They determined that highly mismatched W grain boundaries would explode, with failure occurring during heating in the third or fourth thermal cycles, while small mismatched grain boundary W showed no failure or accumulation of hydrogen in grain boundaries. The authors stated that increasing grain boundary mismatch (to 45°) increases the available sites for hydrogen. During rapid heating, stored hydrogen will then expand and stress grain boundaries that can result in grain boundary explosions (in W bi-crystals). A recommendation was made to use W cladding on cermets, with a vapor deposition technique that allows control of grain boundaries. This explanation for the effect of matrix grain orientation, in which hydrogen at grain boundaries is undesirable, seems potentially at odds with explanations for ThO_2 additions to metal matrices and for use of smaller particle size metal matrices. The suggestion for these effects was that resultant smaller grain sizes improved fuel loss performances by providing increased hydrogen storage sites.

3.2.2.8. Hydrogen pretreatment of particles. Pretreating W and UO_2 particles with H_2 at 1000–1200 °C before consolidation was found to reduce UO_2 losses from W–20 vol.% UO_2 cermets during thermal cycling to 2600 °C in 6.89 MPa static H_2. H_2 pretreatment of W-coated UO_2 particles did not have a significant effect on UO_2 losses during thermal cycling. The effect of heating an impaction assembly (impaction can along with particles) at 1200 °C, either in vacuum or H_2 before pneumatic impaction at 1200 °C, was also tested and found to further improve UO_2 loss performance. The improved performance with H_2 pretreatment was attributed to improved purity of the specimens obtained during H_2 pretreatment. An analysis of the oxygen content of W matrices showed that H_2 pretreatment, in the presence of micronized UO_2, removed about half of the oxygen in the W, and use of flowing H_2 during pre-impaction heating reduced the oxygen content further, but did not completely remove it. It was concluded that H_2 pretreatment removes oxygen from the W matrix and thereby inhibits formation of a ternary W–U–O phase in the W grain boundaries, which may migrate through grain boundaries to the surface and then vaporize [12].

For pneumatically impacted specimens, post-impaction annealing in H_2 significantly reduced UO_2 losses during thermal cycling. The effect of annealing (for 12 h at 1750 °C) on W–20 vol.% UO_2 cermets was particularly beneficial when combined with H_2 pretreatment of particles. Analysis of elemental concentrations of non-annealed and annealed W powder specimens showed that oxygen was reduced by a factor of 20–30 and that carbon content was reduced by a factor of ~4 [12]. When H_2 annealing was completed on W-coated UO_2 particle cermets, namely W–13.3 vol.% (W-coated UO_2), Baker et al. [12] concluded that acceptable UO_2 losses were obtained without H_2 pre-cleaning treatments W particles or pre-impaction heating in H_2. Results for thermal cycling tests to 2500 °C in 4.14 MPa of static H_2 showed ~4% UO loss at 30 cycles for H annealed cermets that were loaded in air. Examination of microstructures after annealing revealed that W coatings and added W particles had recrystallized during annealing. The beneficial effect of annealing was believed to reflect purification (shown by elemental contents of

W–UO_2 cermets) and stress relief (shown by thermal expansion data) [12].

3.2.2.9. Cermet sintering conditions. To prevent UO_2 loss and to preserve mechanical integrity, researchers found that U metal could not be present in the cermet at the time of cladding; it was necessary to ensure that the cermet did not contain UO_2 that was substoichiometric in oxygen [8]. Therefore, 'wet' sintering was studied, in which a slight amount of H_2O was added to the gaseous environment, so that oxygen was available to the cermet material during sintering. Burt et al. [8] studied the effect of wet sintering on cermet fabricated by pressing and sintering (not stated in the report but inferred). They found that (W-clad) W–50 vol.% UO_2 cermet specimens sintered in purified He underwent more thermal cycles without structural deterioration and appreciable fuel loss than did specimens that were sintered in wet H_2. Metallographic examination of a wet H_2 sintered (W-clad) W–50 vol.% UO_2 specimen showed that a small amount of U metal was present in the microstructure. The researchers concluded that sintering cermets in purified He can prevent reduction of UO_2 to UO_{2-x} equally or more effectively than purified H_2 containing 1% H_2O partial pressure. Further investigation on the issue of wet sintering revealed that a 'bulge' was present in a (W-clad) W–52.84 vol.% (UO_2 with 6.93 wt% Gd_2O_3) specimen after wet H_2 sintering. The bulge was believed to be a result of trapped H_2O vapor during sintering. Thus, a method was developed to introduce H_2O to a H_2 sintering environment only after the specimens attained their maximum densification. The improved method, using a 1-h exposure to wet H_2 at 2350 °C, eliminated bulging and was sufficient to reoxidize UO_{2-x} to UO_2 [8]. Collins [21] completed an extensive study on the diametral change of refractory metal–UO_2 cermet with 1200–1800 °C thermal cycling in 0.130 MPa He. All cermet specimens were clad, but were fabricated by a variety of techniques, including variations of dry and wet H_2 sintering. Collins did not observe significant differences in long-term cermet diametral change as a function of sintering conditions; the cladding might have prevented any performance effects from showing [21].

3.2.2.10. Cermet impurity content. Impurities in cermets are thought to react or vaporize when the cermets are heated, which causes defects in the fuel that lead to fuel loss. A example of this effect is a study by Baker et al. [12] on W–20 vol.% UO_2 specimens containing various amounts of C. Specifically, the specimens contained 127 ppm, 71 ppm, 57 ppm, and 32 ppm (no unit) C. The researchers determined that the presence of C at or below 70 ppm caused a significant decrease (<20 wt% versus >35 wt%) in UO_2 loss during thermal cycling to 2600 °C in 6.89 MPa of static H_2 [12].

Removal of oxygen impurities in the W matrix of W–20 vol.% UO_2 cermets improved performance. Improvements in thermal-cycled UO_2 loss performance were attributed to treatments that showed lowered oxygen contents, as well as lowered carbon contents.

3.2.2.11. Cermet density. Saunders et al. [16] stated that W–UO_2 cermet (they recommend W-coated UO_2) should be consolidated to full density; >98% TD for best UO_2 loss performance with thermal cycling. No data, however, are shown in their report to explain this premise. Collins [21] measured the diametral growth of clad (W/25 at.% Re clad) W–(60 vol.% UO_2 with 10 vol.% ThO_2) cermets after thermal cyclic testing to 1650 °C for 4 h in static He and found that the growth for the cermet with 95%–97% TD was at least an order of magnitude less than that of a cermet that was 93% TD (<0.1% versus ~1% diametral change after 60 cycles). The better performing cermet is indicated as containing a 'experimental fuel form of low expansion', which may mean that some unlisted modifications or components account for improved performance and the lower thermal expansion.

3.2.2.12. Cermet cladding. Claddings, a thin layer of material around the cermet core, were fabricated by various techniques to include powder metallurgy methods, hot-rolled foil, gas-pressure bonded foil, plasma spraying, and vapor deposition [16]. Some cursory work was also completed on integral processes, where the cladding is applied as part of the cermet consolidation process. For example, containers or material holding cermet powders prior to consolidation were bonded to the cermet core during consolidation [11,18].

Experiments using claddings of various types were completed to determine if claddings could minimize fuel loss by eliminating surface vaporization loss, slowing reactions that lead to UO_2 and mechanical integrity loss, and reducing the negative effects of the flowing gas environment. Experimenters overwhelmingly determined that claddings significantly reduced UO_2 fuel loss. The success was attributed not only to the mechanisms listed previously, but also to the fact that escaping oxygen (in the form of H_2O) could not easily diffuse outward through W cladding (although H_2 could diffuse inward). Saunders et al. [16] states, in fact, that a study was completed in which it was determined that the rate at which an O:U ratio decreases in a cermet of known composition can be calculated from oxygen permeation data and oxygen partial pressure data and that cermet lifetime is directly proportional to oxygen permeation rate.

Burt et al. [8] showed that unclad W–50 to 60 vol.% UO_2 cermets, with and without a stabilizing addition to the UO_2, exhibited immediate and excessive UO_2 losses during a first thermal cycle to ~2500 °C in H_2, whereas W-clad cermets, having a sound thick W layer, withstood many thermal cycles to 2500 °C without failure. Saunders et al. [16] reported that both gas-pressure foil claddings and plasma spray claddings showed promising results (for plasma spray cladding a 0.5%–no unit specified-UO_2 loss from W–20 vol.% UO_2 tested at 2500 °C for 2 h in H_2); however, the methods did not apply well to complex configurations. GE researchers [22,21], as well as Burt et al. [8], used hot gas-pressure bonding, typically followed by a diffusion treatment, to produce claddings that showed good bonding, which performed well under thermal testing. Lenz and Mundinger [3] used W slurry that was spray-coated onto W–50 vol.% UO_2 for varying numbers of coatings. Specimens thermally tested at 2350 °C for 10 min showed a UO_2 fuel loss reduction from 18.9% (no unit) for a singly coated specimen to 1.4% (no unit) for a triple-coated specimen. A five-coated cermet specimen that was heated to 2600 °C and held for 10 min had a 3.4% UO_2 loss (no unit). Lenz [4] also experimented with vapor-deposited W claddings from a tungsten-carbonyl compound. Tungsten-carbonyl vapor-deposited claddings were found to lower fuel losses during thermal testing by several percent as compared with the W claddings from spray coating. Lenz later deposited W–25 at.% Re claddings by hydrogen reduction of tungsten-halide; these coatings were considered to be of better quality and reproducibility than previous methods. Other researchers [8,26,9] used the W-halide cladding deposition technique, with WF_6 and WCl_6 as the preferred starting materials.

The results of Lenz [4] for (W-clad) W/25 at.% Re–40 vol.% UO_2 show that the thickest cladding of 152 μm (6 mils) performed more than proportionately better for the increased thickness; authors suggested this could be due to increased stiffening of the specimen. Lenz and Mundinger [3] demonstrated that increasing the percentage of cladding to core for (W-clad) (W with 0.17 at.% TiO_2)–50 vol.% UO_2 cermet significantly decreased the percentage of UO_2 lost during thermal testing at 2600 °C. The effect of cladding thickness was also demonstrated by Saunders et al. [16] who conducted experiments on (W-clad) W–20 vol.% UO_2 (with 2.5 mol% Y_2O_3) thermally cycled to 2500 °C in H_2, which contained claddings of various thicknesses. The specimen with a 125-μm cladding showed very gradual UO_2 loss (a couple wt%) up to 120 cycles, while the 25-μm clad specimen showed the beginnings of catastrophic failure at ~10 cycles. Although the thicker cladding improved UO_2 loss performance, microscopy showed that UO_2 migration was not prevented.

Saunders et al. [16] tested the effectiveness of claddings of various coverage (none, face clad, and fully clad). Cladding greatly reduced UO_2 losses in cermets after 10 cycles to 2500 °C in H_2; the disparity in UO_2 loss between unclad and (W-face-clad) W–20 vol.% UO_2 was approximately an order of magnitude. The difference in UO_2 loss between (W-face-clad and fully clad) W–35 vol.% UO_2 cermets was also ~1 order of magnitude after 10 cycles, but became much greater with more cycles. Researchers concluded that a 25-μm-thick W cladding fully covering a W–20 vol.% UO_2 cermet was sufficient to reduce UO_2 loss to <1% (no unit) for W–20 vol.% UO_2 heated to 2500 °C for 2 h in H_2.

A number of cladding compositions were studied, including W, Mo, Re, Ta, Nb, and alloys thereof. The success of the cladding was dependent upon the cermet cladding composition relative to the core composition (assuming that the cladding was well bonded to the core). Newsom and Danforth [23] observed Kirkendall voids at cladding/core interfaces, which were a result of differential diffusion rates between differing materials, for Nb-clad Mo–60 vol.% UO_2 after simultaneous thermal cycling and radiation testing at 1760 °C in 0.1 L/min He. Cracking and cladding/core separations, attributed to thermal expansion mismatch and ductility differences between the cladding and core, were observed for (W/30Re/30Mo clad) W–54 vol.% (UO_2 with 6 vol.% ThO_2) cermets that were thermal cycled and radiation tested at 2000 °C in He and at 1650 °C in He + 5% H_2 (no unit), respectively.

3.2.3. Metal matrix variations

Metals that are both sufficiently refractory for ‘high-temperature’ cermets and are available in quantity are W, Mo, Ta, and Re. While most high-temperature cermet studies focused on W–matrix cermets, some alternatives were studied. Researchers, particularly Lenz, hypothesized that use of cermet refractory metal matrices that were more ductile than pure W could improve mechanical integrity during thermal excursions of cermets with claddings and would therefore reduce fuel loss. Several matrices were studied for that purpose, specifically metals and alloys of Mo, Re, and W.

3.2.3.1. Mo and Mo alloys. Lenz et al. [2] completed considerable work on the characterization of the Mo–UO_2 cermet system. While most of the studies did not include direct comparisons with other refractory metal matrix cermets, a few comparisons do exist. Lenz and Mundinger [3] found that after thermal testing at 2350 °C in H_2, (Mo with 0.6 at.% TiO_2)–50 vol.% UO_2 cermet resulted in much better visual mechanical integrity as compared with (W with 0.6 at.% TiO_2)–50 vol.% UO_2, but UO_2 loss was ~25% greater for the Mo-based cermet. No clear explanation was given for these mixed results, although the authors did mention that a more ductile matrix should prevent the cracking tendency. Collins [21] compared geometrical and weight changes for refractory-metal-clad W–60 vol.% UO_2 and refractory-metal-clad Mo–60 vol.% UO_2 cermets thermally cycled to 1200–1800 °C for as many as 34 cycles in 0.130 MPa static He. Under the conditions of the test, all the cermets performed well and similarly (almost all <1% geometrical and weight change).

3.2.3.2. Re and Re alloys. Additions of Re to the refractory matrix did not clearly improve thermal performance. Thermal testing on (W/15 to 25 at.% Re with and without TiO_2)–50 vol.% UO_2 resulted in UO_2 losses that were comparable to or greater than pure W–50 vol.% UO_2 after thermal cycling to 2350 °C in H_2. However, visual testing showed that Re additions greatly improved mechanical integrity of the cermet; a pure W-based specimen was badly crazed, while W/Re-based specimens were mostly sound, with one specimen showing slight crazing. Addition of a W-carbonyl cladding to W/25 at.% Re–50 vol.% UO_2 cermet resulted in UO_2 losses of less than 3% (no unit) and no crazing after 20 min in H_2 at 2650 °C [3]. Collins and Newsom [20] compared performance for W–60 vol.% UO_2 and W/5 vol.% Re–60 vol.% UO_2 cermets with claddings of W/25 at.% Re/30 at.% Mo. The cermet with the Re matrix addition showed initially higher diametral growth with thermal cycling to 1800 °C, but also a slower growth rate, so that its diametral growth was surpassed by that of the W matrix-only cermet at ~85 cycles. In the study described earlier for Mo containing matrices, Collins [21] compared geometrical and weight changes for cermets containing different refractory metal matrices, including Re. The Re matrix cermets performed well, but not markedly different from other matrix cermets. A study by Lenz [4] comparing (W/30 at.% Mo/12 or 17 at.% Re)–40 vol.% (UO_2 with 4 vol.% Y_2O_3) after cycling to 2600 °C in flowing H_2 showed that catastrophic UO_2 losses occurred more rapidly for matrices with the lesser amount of Re.

4. Radiation performance

4.1. Fission effects on cermet material

During performance, a fissile fuel will fission and be consumed or ‘burned up’. During fuel burnup, fission products are formed and energy is released in the form of heat. These activities can produce effects upon the fuel material microstructure and macrostructure. For high temperature fissile fueled cermets, the predominant effect is dimensional growth.

4.1.1. Fission products

As fuel fissions, two major effects occur, both of which lead to swelling of a cermet. First, solid products are formed that are lower in density than the surrounding material, and second, gaseous products are formed with an associated pressure. At sufficient levels, the gas pressure results in elastic, plastic, and creep deformations of the cermet.

Fission products that are produced from burnup of a fissile fuel material are a function of both the energy level of the neutron flux that produces fission and temperature. As operating temperature increases, more of the fission products are above their boiling points; hence, the higher the temperature, the greater the proportion of fission products that are in a gaseous form. A calculation for relative contributions of solid and gaseous fission products for a W–60 vol.% UO_2 cermet at a constant pressure and various temperatures shows that the gaseous proportion of the products clearly increases at a rapid rate when increasing from 1427 to 1649 °C [24].

4.1.2. Steps in fission product swelling

Several steps are common to the growth process resulting from fission gas swelling. Initially, fission gas pressure increases linearly with time. As gas pressure becomes greater, creep deformation of the cermet occurs and produces significant growth of the cermet (i.e., an increase in porosity). As porosity levels increase, the fission gas pressure decreases and can eventually reach negative levels. During this process, stresses in the cermet increase and finally reach a limiting value that is a function of creep properties of the cermet and the rate of generation of gaseous fission products. Stresses are initially compressive due to the external system pressure on the fuel element. Growth of the cermet is initially zero, but quickly increases as fission gas pressure increases and the cermet creep strength is exceeded. As stresses reach their limiting values, growth also approaches a final value [24].

4.2. Experimental effects on radiation performance

4.2.1. Test condition effects

4.2.1.1. Fissioning. Modeling results by GE [24] showed the effects of fissioning on cermet stability. Nominal parameters for the modeling were W–60 vol.% UO_2 cermet with a density of 95% TD, and test conditions of 1538 °C, a system pressure of 1.38 MPa, and a burnup rate of 1×10^{20} fissions/cm^3 matrix (1.67×10^{20} fissions/cm^3 fuel). As the number of fissions increased, growth increased, as well as growth rate. For example, at 0.8×10^{20} fissions/cm^3 of matrix, the diametral growth was less than 1.5%, even up to 10000 h of burnup time. At 1×10^{20} fissions/cm^3 of matrix, the diametral growth was ~2.3% at 10000 h. At even greater burnup levels of 1.2×10^{20} fissions/cm^3, the diametral increase was almost 3% at 6000 h. The largest increase for any of the specimens was during the first 4000 h of burnup, typically accounting for ~75% of the total diametral growth; the final ~25% of total diametral growth occurred during the last 6000 h of burnup (for the cermets at 0.8×10^{20} and 1.0×10^{20} fissions/cm^3 of matrix tested to 10000 h) [24].

4.2.1.2. Temperature with radiation. Extensive experiments were completed to test the effects of both temperature and radiation on test configurations containing W alloy clad W–60 vol.% UO_2 cermet pieces (97% TD, metallurgically bonded, and unvented). Data showed that the test configurations could be operated to definite temperature-burnup conditions before blisters developed, with subsequent cladding rupture and release of fission gases. For example, a (W/30 at.% Re/30 at.% Mo clad) W–60 vol.% UO_2 cermet was sound (as determined by dimensional stability and gas analysis for fission products) up to a burnup level of 6.7×10^{19} fissions/cm^3 of cermet and temperatures up to 1440 °C in He with 5% H_2 (no unit) at a thermal neutron flux of $3–3.9 \times 10^{12}$ neutrons/cm^2 s. Increasing the operating temperature from 1440 °C to 1500 °C reduced service capability by ~20%.

Microstructural analysis of the tested clad W–UO_2 cermets specimens showed that metal matrices and UO_2 fuels were structurally stable with no channeling or formation of additional phases. The W and UO_2 phases remained dense except for fission gas bubbles that formed within the grain boundaries of the UO_2. Fission gases (10–20%, no unit specified, presumably atomic percent) that were generated during irradiation were found to be mobile through interconnected porosity. Several specimens showed voids at the cladding/core interface that were attributed to the Kirkendall effect, including specimens composed of (Ta clad) W–UO_2/ThO_2 and (Nb clad) Mo–UO_2/ThO_2. (W/30 at.% Re/30 at.% Mo clad) W–60% UO_2 specimens showed not only voids, but also an intragranular sigma phase in the cladding [22].

4.2.2. Fabrication condition effects

4.2.2.1. UO_2 particle size. Riley and Taub [6] irradiated (W clad) Mo-40–60 vol.% UO_2 cermets made with various UO_2 particle sizes. Fine UO_2 particles (several μm diameters) were found to coalesce during irradiation to particle diameters that were ~10–30 μm. The coalescence did not occur during normal sintering. As a result, the cermets shrank considerably and desired porosity was no longer present. Cermets containing UO_2 particles with large diameters (>100 μm) showed fracturing of the UO_2 when irradiated. Cermets containing medium sized UO_2 (20–30 μm) particles showed the most promising results, particularly when used at loading levels in which the UO_2 particles were not interconnected and therefore could not coalesce.

4.2.2.2. UO_2 fuel loading. Increasing the amount of fuel (UO_2 particles) from 20 to 40 vol.% had little effect on diametral growth; the growth only changed from 0.25% to 0.5%. However, increasing the UO_2 content from 40 to 70 vol.% caused the diametral growth to increase from 0.5% to 4% [24].

4.2.2.3. Metal matrices. Newsom and Danforth [23] exposed (Nb clad) Mo–60 vol.% UO_2 cermet to simultaneous thermal testing at 1760 °C, irradiation testing at $4–5 \times 10^{12}$ neutrons/cm^2 s, and flowing inert gas for 855 h. The ^{133}Xe fission gas release fraction for the Mo–UO_2 was greater than for W-based matrix specimens by 1–2 orders of magnitude, however, the Nb clad Mo–60 vol.% UO_2 specimen was generally sound, the fuel was stable, and the core–cladding bond was maintained. A relatively minimal amount of void formation occurred at the core-cladding interface, and there was evidence of fission gas products collected into grain boundaries of the UO_2.

Newsom and Collins [21] completed testing on W/Re matrix cermets with more complex structures that contained multiple numbers of cermet specimens. Test conditions included a thermal neutron flux of 3.0×10^{12}–3.9×10^{12} neutrons/cm^2 s, He with 5% H_2 (unit unspecified) at 0.14 kg/mm^2, and a temperature range of 1150–1550 °C. Results showed that use of a W–3 vol.% Re alloy matrix did not extend the leak free life of the cermets or minimize blister formation, but was actually detrimental to performance. Furthermore, W–Re based cermet grew approximately twice as much as unalloyed W based cermet during thermal testing. The excessive growth was attributed to a lower creep strength and thus greater creep rates for the more ductile W–3 vol.% Re alloy as compared with pure W, and was considered a means for loss of fission gases. Newsom and Collins concluded that the burnup at 1440 °C before fission gas loss and blister formation occurred, was 10% greater for cermets containing unalloyed W matrix as compared with cermets containing a W–Re matrix [22].

4.2.2.4. Cermet density and porosity. Density showed a strong influence on growth. For example, modeled results by GE [24], in which density for W–60 vol.% UO_2 was increased from 90% to 100% TD, showed increased diametral growth from 0.5% to almost 5% (1538 °C, system pressure of 1.38 MPa, and a burnup rate of 1×10^{20} fissions/cm^3 matrix–1.67×10^{20} fissions/cm^3 fuel). Volumetric growth for 100% TD cermet increased by ~14.5 vol.% while 95% TD cermet showed ~8 vol.% growth at 10 000 h. Both 95% TD specimens swelled less than or equal to 2 vol.% at 6000 h [24].

Increasing porosity levels was found to improve cermet service capability. In particular, however, interconnected porosity gave the greatest performance. Ranken and Reichelt studied the effects of radiation on (W clad) Mo–40 vol.% UO_2 cermets, using a power density of 216–365 W/cm^3 at ~2000 °C to a maximum burnup of 3.6×10^{20} fissions/cm^3 of cermet. Diametral growth decreased with increasing interconnected porosity, decreasing temperature and decreasing irradiation time. A value of 271 830 kJ/mol for the activation energy of creep during irradiation was calculated [7].

4.2.3. Fission gas location

The concentration of the fission product ^{85}Kr in (W clad) Mo-40 vol.% UO_2 cermet specimens as a function of location was studied. The specimens were 86–93% TD with a interconnected porosity of 4–13%. ^{85}Kr content was found to increase at locations more near the center of the specimen. Researchers determined that fission gas retention in the UO_2 phase of the cermet was the most important cause of dimensional increase. This retention amounted to ~3–10% increase in length after 10,000+ h of irradiation, depending upon the different UO_2 particles used in the cermet and the interconnected porosity levels. Fission gas retention in the Mo matrix (introduced by fission recoil) was determined to be an unimportant source of dimensional increase. A value of 271 830 kJ/mol for the activation energy of creep during irradiation was calculated [7].

5. Summary

Many variables will affect the lifetime of the cermets; some of these are parameters that are not necessarily controllable, i.e., operation conditions, but other parameters are fairly easily controlled. For example, many composition modifications can be used to improve fuel loss performance. Of all the controllable parameters, use of a cladding that was chemically and mechanically compatible with the cermet core seemed to produce the most significant performance improvements. Coating UO_2 particles with the matrix metal was typically as effective as cladding the cermet; both techniques were capable of reducing fuel losses to <1% (unit unspecified). Other important variables that generally improved performance included the addition of a stabilizing oxide to UO_2, controlling the UO_2 particle size, coating the UO_2 particles, adding ThO_2 to the metal matrix, fabricating the cermet from smaller metal matrix particles, minimizing impurities, using H_2O in the cermet sintering atmosphere at appropriate stages, annealing consolidated cermet in H_2, and controlling the cermet density. Parameters that provided best thermal performance typically corresponded with parameters for best radiation performance, but this was not always the case. Density levels were a notable example, where greater theoretical density ($\sim > 95\%$ TD) gave best thermal performance, but lower density gave better radiation performance.

Saunders et al. [16] stated that their preferred technique for fabricating a W–UO_2 cermet with minimum fuel loss after thermal cycling would include use of W-coated (by hydrogen reduction of WCl_6) and Ce_2O_3 stabilized UO_2 particles of a fine diameter (i.e., ∼1 μm) in a W matrix that contained an addition of ThO_2. The cermet would be consolidated to full density (>98% TD), preferably by pneumatic impaction or hot isostatic pressing, and would be clad with a thin layer (25 μm minimum) of W using hydrogen reduction of WCl_6 [16]. A summary report by ANL gives the following suggestions: use of oxide stabilizers, preferably Gd_2O_3, Dy_2O_3, or Y_2O_3 to the UO_2, use of a W coating on UO_2 particles, use of optimum sintering parameters including temperature, time, and H_2/H_2O concentrations during sintering, minimizing C, free U, and F, and use of a sound, 180–230 μm W or a W/25 wt% Re cladding [1].

Variations on the W–UO_2 cermets in the studies reviewed included use of Mo, Re, or alloys in place of W. The alternative metal matrices showed some mixed results and did not typically perform significantly better than W.

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