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Hydrogen Corrosion Considerations of Carbide Fuels for Nuclear Thermal Propulsion Applications

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At reactor operation conditions of interest for nuclear thermal propulsion (NTP), graphite- and carbide-based fuel materials have been known to exhibit a number of life-limiting phenomena. These include the formation of liquid, loss by vaporization, creep and corresponding gas flow restrictions, local corrosion, and structure degradation due to excessive mechanical and/or thermal loading. In addition, the irradiation environment can cause a substantial change in the local physical material properties, which can produce high thermal stresses and corresponding stress fracture (cracking). Time–temperature history and cyclic operation of the nuclear reactor can accelerate some of these processes. Based on results of a review of open literature, available in the U.S., a number of major competing interrelated physical mechanisms were identified that affect hydrogen corrosion of carbide fuel materials. This article identifies and discusses in detail these mechanisms associated with the corrosion of carbide-based materials when exposed to hot hydrogen flow at conditions typical of NTP reactors. From the understanding of this complex phenomena, modeling requirements are then identified and discussed.

I. Introduction

NUCLEAR thermal propulsion (NTP) engine systems are attractive options for orbit transfer and planetary exploration applications because they typically exhibit a specific impulse over twice that associated with chemical propulsion systems.[1–3] To achieve such a performance gain, hydrogen is used as the NTP engine system working fluid propellant because of its low molecular weight. Hydrogen, at pressure, is heated in an NTP nuclear reactor to high temperature before it is expanded through a supersonic nozzle to create thrust.

Hydrogen temperatures and pressures in an NTP reactor chamber are typically greater than 2500 K and 3 MPa, respectively. Since NTP engine system specific impulse is directly proportional to the reactor chamber temperature, engine systems that operate at chamber temperatures in the range of 3000 K or greater are of great interest because they reduce overall mission launch (infrastructure) weight requirements and corresponding cost.[1–5] Additionally, to minimize mass, which is a key consideration in any space system design, NTP reactors operate at high-power densities. Power densities of up to 2.7 MW/l have been demonstrated, while next-generation solid-core reactor concepts could operate at power densities greater than 10 MW/l for single burn, short operation time applications.[4,5] Operating at these high-power densities produces a high radiation flux environment in the reactor core. To meet this engineering challenge, uranium–zirconium–carbon (U–Zr–C) and uranium–niobium–carbon (U–Nb–C) material systems have been considered for such applications.[4–11] Exposure to high nuclear radiation, plus the other operation conditions just mentioned, provide an extremely hostile environment for NTP reactor core materials. Carbide material systems are considered in NTP reactors due to their favorable nuclear properties [relatively small absorption nuclear cross section(s)], high melting point, thermal stability, low volatility, high fuel fraction, high moderation ratio, and low density (<10 g/cm^3).[12]

At the operation conditions of interest in NTP reactors, graphite-based fuel materials have been known to exhibit a number of life-limiting phenomena.[4,6–8,11,12] These include the formation of liquid, loss by vaporization, creep, and local corrosion. Substantial fuel structure degradation and/or mass loss can result from these material interaction phenomena. The high chemical reactivity (corrosion) of carbon when exposed to hot hydrogen was well known at the start of the NTP development program in the early 1960s.[4,6–8,11,12] Thus, many of the NTP fuel designs pursued have incorporated high-temperature, corrosion-resistant coatings, such as ZrC, NbC, TiC, and Mo thin surface coatings.[4,6–8,11,12] Typical fuel design compositions considered for the Rover and Nerva programs included small UO_2 or UC particles coated with ZrC dispersed in a carbon graphite matrix that was also coated with a thin NbC or ZrC surface coating.[4,6–8,13] The integrity of these complex fuel designs has been challenged by many of the combined (coupled) effects of reactor environmental and design operational factors, such as excessive mechanical and/or thermal loading and nuclear radiation exposure.[4,6–8,11] The high-radiation environment associated with NTP reactor operation was found to cause a substantial change in local physical properties of the fuel materials, producing high thermal stresses that contributed to the stress fracturing (cracking) of the surface coating and/or the fuel form. Such observations were initially considered surprising because of the low reactor burn-up that is typical of NTP system operation.[4,6–8,11] It has also been observed that time-temperature history and cyclic operation of the nuclear reactor can accelerate many of these processes.[4,6–8,11] Because of these design/operation issues exploratory research was performed, near the conclusion of the Rover program, that examined by experimental reactor test-

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ing highly integral composite graphite and solid-solution carbide [(U,Zr)C] matrix fuel element designs.[4,6–8,13]

Degradation of the nuclear fuel integrity by the physical processes just mentioned has been the subject of research and development during reactor testing associated with the Rover and Nerva programs.[4,6–8,11] Of most concern was the core material mass loss associated with corrosion of the prismatic design fuel elements used in these programs. Material mass loss occurred at temperatures substantially lower than the fuel material melting temperature (2500 K at 60-min life vs 3200 K), and accounted for a large percentage of the core material loss during operation. Much of this fuel mass loss observed from Rover/Nerva program test data was attributed to the corrosion of the graphite by hydrogen, releasing the coated UO_2 or UC particles.[4,6–8,13] These highly complex phenomena, encompassing many of the life-limiting processes previously discussed, made engineering solutions to correct this problem difficult to identify and implement. The hydrogen corrosion process substantially reduces NTP engine system performance and life, which directly influences overall mission safety, reliability, and cost.

An extensive review of U.S. open literature was performed that examined the complicated hydrogen corrosion process of graphite-based nuclear fuel materials of interest to NTP reactors.[13] This article draws substantially on the results of this past work and provides detailed insight into the hydrogen corrosion issue associated with NTP reactor systems, as well as its impact on engine system design. Much of the discussion focuses on the design and corrosion issues of U–Zr–C material fuel systems for NTP reactor applications, but it is also considered relevant to other related high-temperature carbide-based fuel materials.

In this article the competing physical processes associated with the hydrogen corrosion of carbides are discussed in some detail. It should be noted that little hydrogen/carbide material compatibility data are available at operating conditions of interest to NTP reactor systems.[13] Thus, the experience base associated with NTP graphite-based reactor fuels is used, when appropriate, to formulate (identify), and substantiate, likely hydrogen/carbide material corrosion physical process mechanisms. The thermodynamics of representative carbide material systems are also addressed to provide greater insight into carbide material physical states and properties, its operation limitations, as well as the reaction kinetics of carbides in flowing hot hydrogen. The state-of-the-art modeling (prediction) of hydrogen corrosion of carbide material systems is examined to establish the requirements for further research work in this area. Development and application of an accurate corrosion model(s) will allow future NTP reactor systems to be optimized in terms of performance, weight, and lifetime.

II. Corrosion and Interrelated Processes

Observations of NTP graphite-based fuel materials exposed to hot hydrogen showed that many interrelated, competing physical processes that were at work have degraded the structural integrity and/or produce mass loss of these materials. Review of past Rover and Nerva program data indicated that hydrogen corrosion, in general, depends on the following parameters: 1) operation time, 2) duty cycle (on–off cycles), 3) local material temperature, 4) local gas flow conditions, 5) fuel material location in reactor, 6) reactor power density, and 7) fuel material/coating design compatibility.[6–8,12,13] From first principles, one expects corrosion to be highest at the local maximum surface temperature of the fuel material. This expectation was not found to be the case, as is shown in Fig. 1.[7,8] In Fig. 1, the maximum mass loss rate typically occurred in the moderate temperature region (<2000 K) of an NTP fuel element. This observation, plus others from posttest inspections, indicated that numerous competing processes are at play.

Based on the NTP graphite-based fuel materials experience, many competing hydrogen corrosion physical process mechanisms associated with carbide fuels can be identified. It should be remembered that past Rover and Nerva programs principally examined fuels that were composed of small UO_2 or UC particles coated with ZrC dispersed in a carbon graphite matrix that was also coated with a thin NbC or ZrC surface coating. This can be contrasted to a typical high-temperature NTP carbide fuel material, which is a binary or ternary solid-solution matrix composed of UC, ZrC, U–Zr–C, or U–Nb–C. Because of the potential high-temperature capability associated with a carbide material, coating of surfaces exposed to hydrogen is, typically, not considered. These differences and similarities, between graphite-based and carbide-based fuel forms, should be kept in mind as one examines hydrogen corrosion of carbide and related material systems.

A schematic of hydrogen corrosion phenomena of carbide fuels that displays its many interrelated, competing physical processes is shown in Fig. 2a (also see Figs. 2b and 2c). There are four major coupled, reaction and/or healing (slowing down) processes that drive corrosion. They are 1) exposure to hydrogen gas, 2) nonuniform loading and/or cycling of the fuel material, 3) radiation exposure, and 4) creep of material defects. These processes interact with each other, depending on the local conditions, and the fuel design. The first physical process listed is directly associated with the actual transport/chemical corrosion reaction mechanisms that are responsible for the mass loss of fuel material. The other physical processes, while not directly related to the corrosion reaction process, greatly influence the fuel material surface area exposed to the hydrogen gas, which in turn impacts the magnitude (and rate) of fuel material mass loss. It is essential that these fundamental physical interrelated processes be well understood and be considered, where appropriate, in future corrosion modeling efforts. These processes are discussed in more detail in the following subsections.

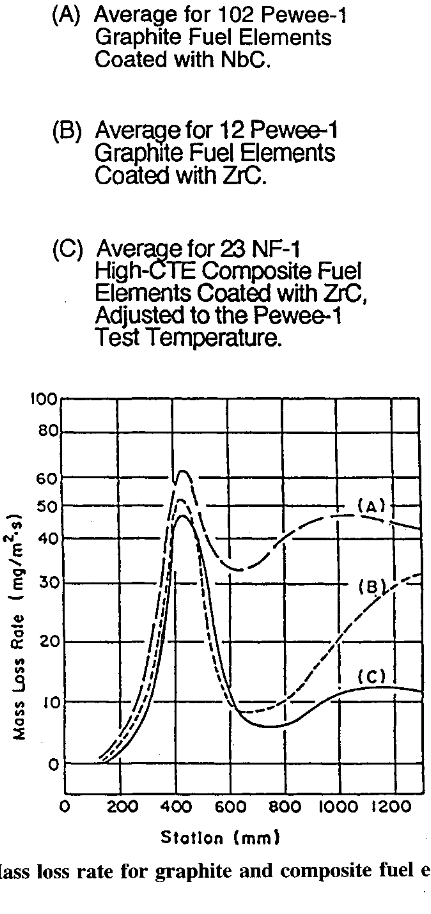
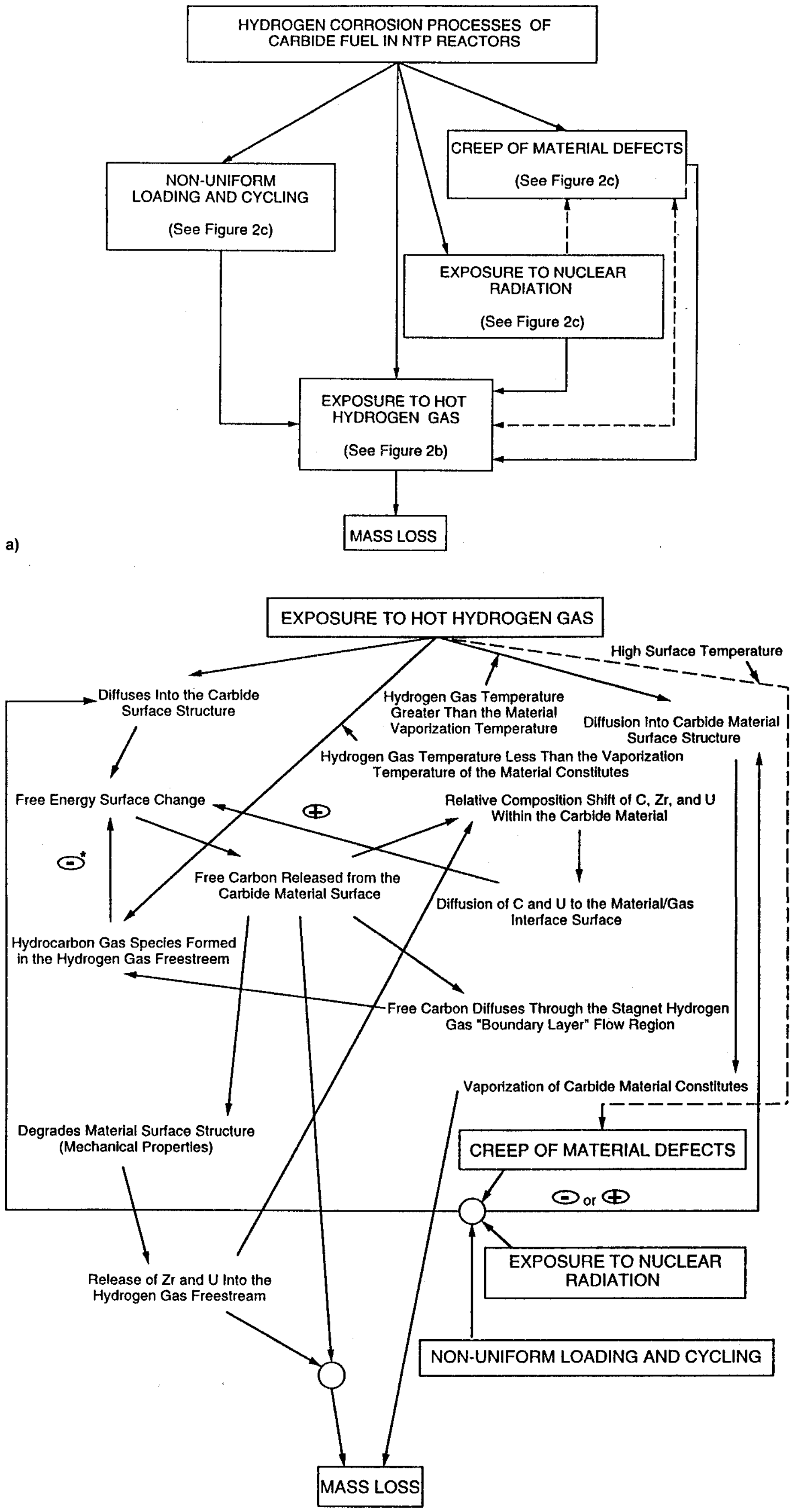
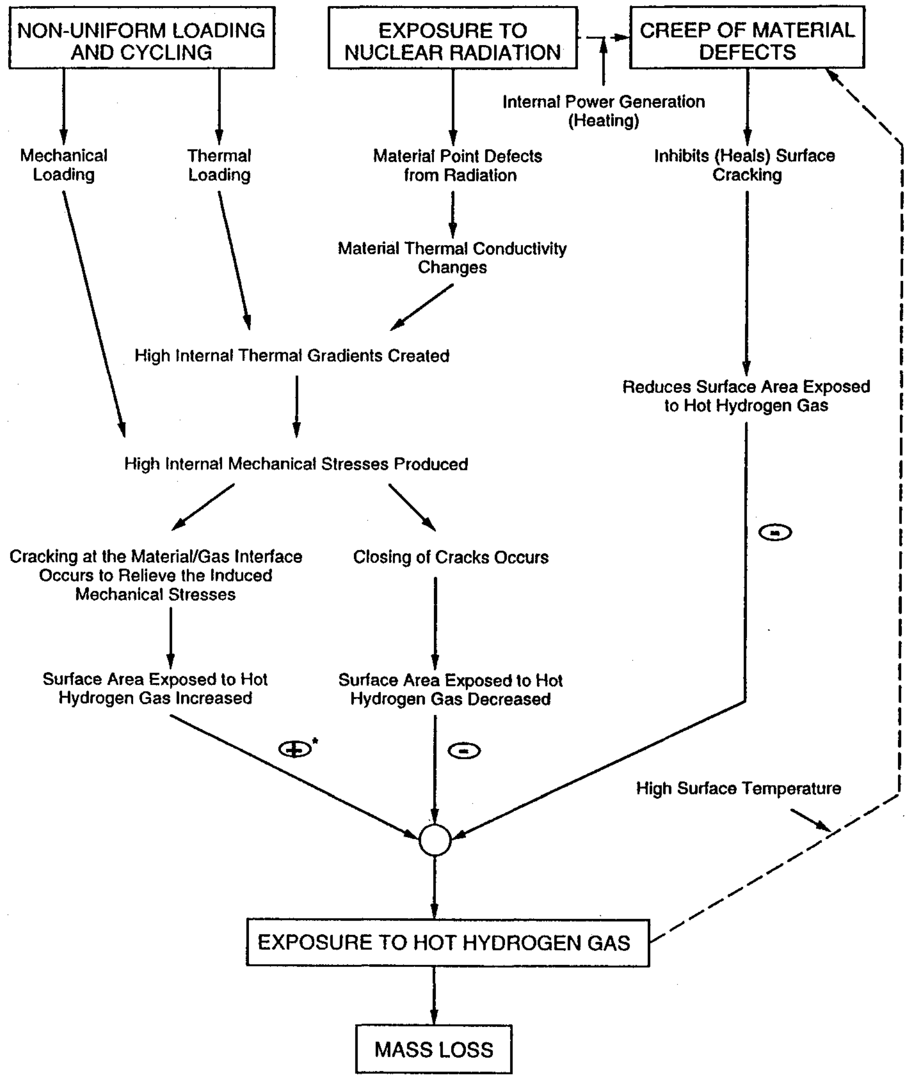


Fig. 1 Mass loss rate for graphite and composite fuel elements.[7,8]



b) *NOTE: ⊕ = Enhanced Mass Loss; ⊖ = Reduced Mass Loss

Fig. 2 a) Schematic representation of the major interrelated physical process mechanisms that influence hydrogen corrosion of carbide fuel, b) hot hydrogen gas exposure, and c) nonuniform loading and cycling, nuclear radiation exposure, and creep of material defects.



c) *NOTE: ⊕ = Enhanced Mass Loss; ⊖ = Reduced Mass Loss

Fig. 2 (Continued) a) Schematic representation of the major interrelated physical process mechanisms that influence hydrogen corrosion of carbide fuel, b) hot hydrogen gas exposure, and c) nonuniform loading and cycling, nuclear radiation exposure, and creep of material defects.

A. Exposure to Hot Hydrogen Gas

Carbide-based fuel materials when exposed to hot hydrogen can experience mass loss by two mechanisms, depending on the local temperature of the material and/or the chemical composition of the flowing gas stream. These mechanisms are 1) diffusion and chemical reaction of the carbide material constitutes with the hot hydrogen gas stream and 2) vaporization (sublimation) of the material constituents. For temperatures less than 1500 K, little, if any, chemical reaction between hydrogen and carbide material takes place. However, at temperatures typically between 1500–2900 K, which is well below the vaporization temperature of candidate NTP carbide-based fuel materials, the chemical reaction process branch (Fig. 2a) will predominate. This corrosion process is highly complex and has been studied in the past in some detail.[14,15]

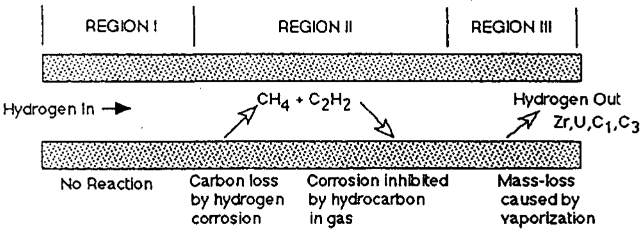


Fig. 3 Hot hydrogen interaction process along a U-Zr-C material duct (not to scale).[14]

In this process the hot hydrogen gas interacts with both the material substrate and with the freed surface products (Fig. 3). For example, carbon forms hydrocarbon gas species byproducts, such as CH_4 and C_2H_2, in the hydrogen-gas freestream. The released free carbon at the surface must first diffuse through the low-velocity/stagnant hydrogen gas boundary layer for hydrocarbon species formation to occur. The formation of hydrocarbons will be affected principally by the local temperature, and to a lesser extent the pressure of the hydrogen gas, as shown in Figs. 2 and 3.[14–23] Based on thermodynamic equilibrium considerations it has been shown in a recent study,[24] at low-to-moderate pressures with temperatures greater than 1500 K, that the formation of CH_4 becomes increasingly unstable. While at these conditions the presence of C_2H_2 was found to be stable. At higher pressures the opposite was found to be true.

The gas flow structure as well as the replenishment of fresh (clean) hydrogen can also impact the corrosion process. Rover and Nerva reactor fuel elements operated at Reynolds numbers, based on the diameter of the coolant channel diameter in the fuel element, in the range of 10^4 correspond to the high-mixing, turbulent-flow region. Radial-flow, packed-particle (or pellet) bed reactors[25–27] also operate in the turbulent flow region. It should be noted that during startup, shutdown, and/or throttling, the transient flow structure within the reactor core could be in the laminar or the transition flow regime, which could also affect the corrosion of the fuel material.

These fundamental corrosion processes are initiated as hot hydrogen gas comes in contact with the carbide material surface structure. Due to the small size of the hydrogen gas species, which is present in significant quantities in both molecular and dissociated forms at the temperature range of interest, it is possible for them to diffuse into the material. Small cracks present in the fuel elements' outer surface that is exposed to the hydrogen gas flow will only enhance the influence of these processes by increasing the exposed surface area (see Fig. 4). At the surface, the material composition changes owing to Le Chatalier's principle of minimum free energy.[14,15,28,29] This composition change is due, in a sense, to the differences in the equilibrium partial pressures of the constituents of the system, i.e., vaporization occurs incongruently. The partial pressure of predominant chemical reaction species of such a system, which includes U(g), Zr(g), and various hydrocarbons, is displayed in Fig. 5.[15] Partial-pressure relationships of the reaction species of interest are discussed in more detail in Refs. 14 and 15. For U–Zr–C material systems, the change in surface chemical composition will likely release free carbon from the surface. This reaction process was known to be prevalent during initial Rover and Nerva program reactor startup operations and is the predominate mass loss mechanism for this corrosion process branch. The fuel elements used in these programs were hyperstoichiometric ("rich") in carbon in order to enhance their productibility during fabrication.[7]

Mass loss by corrosion may also degrade the fuel structural (mechanical) surface properties and physically loosen or erode the fuel by removing particles, such as grains or agglomerations containing Zr and U, from the surface.[6,7] These particles are swept away into the gas freestream. Thus, material mass loss is enhanced even further. Due to the heavy molecular weight associated with Zr and U, a small material loss percentage can represent a high percentage of the overall mass loss. This was found to indeed be true in some past Rover and Nerva tests.[6,7]

In addition to the released free carbon, the surface composition changes, as shown in Fig. 2a. This tends to enhance the diffusion of C and U to the surface owning to the shift in the U/Zr/C ratio at the surface. At locally high temperature, the diffusion of C and U can be substantial, particularly in the vaporization corrosion-controlled process, which is discussed later. This mechanism drives the free energy change at the surface, releasing additional free carbon into the hydrogen gas stream. Conversely, this release of carbon leads to a change in fuel surface composition. This in turn changes the free energy of fuel surface/hydrogen gas boundary-layer reacting system locally. As the local free energy of the material changes due to the rapid release of free carbon, in particular, hydrocarbon gas species are formed, as previously mentioned. The presence of these hydrocarbons tends to reduce the release rate of free carbon downstream, decreasing the rate of fuel material mass loss.[14–16] It is believed that this effect provides a partial explanation for the lower mass loss rates observed at the downstream, high-temperature positions on the fuel elements (Fig. 2a) compared to the mass loss at the lower temperature, upstream positions.

While mass loss occurs, to a varying degree, by the vaporization process in the moderate-to-high-temperature range, it is typically the predominate mechanism of mass loss for U–Zr–C material at surface temperatures greater than 2900 K. Hydrogen diffuses into the exposed hot carbide material surface causing its constituents such as Zr, U, and C, to react. These reaction product constitutes will likely form other compounds such as CH_4, CH_3, C_2H_2, or ZrH, depending on the local material composition and operating conditions considered. In Fig. 6, the recession rates of U, Zr, and C are compared to other uranium compounds and stable refractory carbide materials as functions of temperature.[30] The large recession rates of these high molecular weight compounds correlate into high mass loss rates. At the high temperatures associated with this corrosion process, the high diffusion rate of C relative to

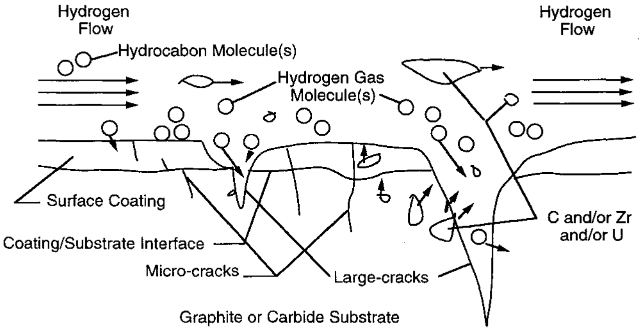


Fig. 4 Effects of surface cracks on corrosion (not to scale).

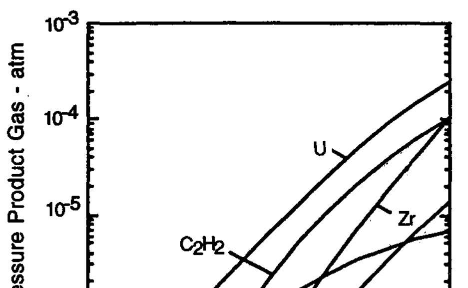


Fig. 5 Equilibrium partial pressures of product constitutes above $U_{0.05}Zr_{0.95}C_{1.07}$ in 1 atm of hydrogen as a function of temperature.[15]

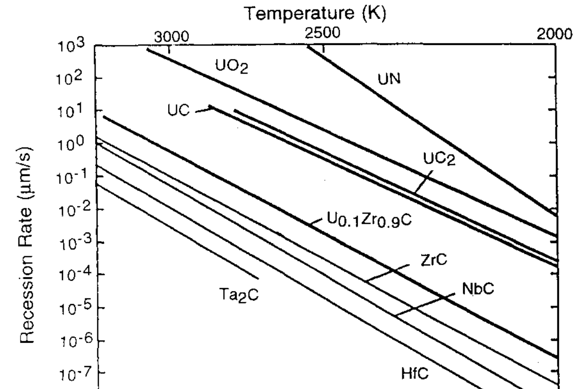


Fig. 6 Recession rate of $U_{0.1}Zr_{0.9}C$ compared to other uranium compounds and stable refractory carbide materials as a function of temperature.[30]

Zr and U (which are approximately the same), promotes its movement to the surface.[14,15,31] Additionally, the large shifts in surface composition would locally change the carbide material's phase properties, which can lower or raise their melting points, depending on the initial composition and the shift in the surface congruent vaporization composition during NTP system operation. Based on past nuclear furnace–1 (NF–1) composite fuel element data (Fig. 7), the mass loss rate in the high-temperature, vaporization region has been reasonably correlated as a function of temperature at realistic NTP operating conditions.

In the vaporization loss region, hydrocarbon species would also be present in the bulk gas stream due to the hydrogen/free carbon reactions that occur upstream (Fig. 3). The presence of hydrocarbons tends to reduce the vaporization rate of the fuel/carbide surface material.[14,15,28] High mass loss rates were not observed at the high-temperature axial positions in the Rover and Nerva fuel elements (Fig. 1). However, it is highly probable that other competing corrosion processes helped control material mass loss in this high-temperature operating regime. An example of such a process is reduction (healing) of material defects by creep, which occurs readily at high temperatures. This phenomenon can help relieve surface coating/fuel substrate interface stresses, which in turn reduces surface coating cracking, and, hence, the rate of mass loss (Fig. 2a). Alternatively, the healing effect of creep can be hindered by the stresses caused by atom(s) dislocation and defects induced by the exposure to nuclear radiation, particularly by the interaction of fast neutrons with the material.[29,32]

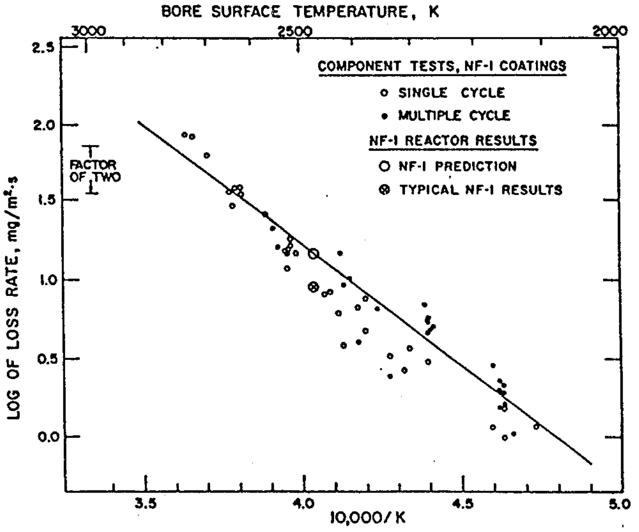


Fig. 7 Component and NF–1 reactor test results for hot-end mass loss rates of composite elements, (mass rate is based on a square meter of fuel element coolant channel surface area).[8]

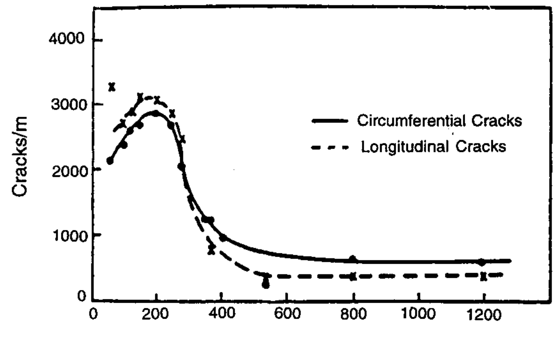


Fig. 8 Number of cracks in ZrC coolant channel coatings as a function of length for a NF–1 composite fuel element.[8]

It should be noted that the presence of material defects can reduce the local thermal conductivity of the material, producing locally high thermal stresses and corresponding surface coating/fuel substrate stress mismatches. Such conditions encourage the formation of surface coating cracks and sequentially accelerates material corrosion. Substantial surface coating cracking was believed to be present during operation in modest temperature, high-radiation flux regions of the Rover and Nerva program reactor fuel elements.[6–8,29] Due to the hostile operation environment, which is characteristic of such reactors, no direct measurement(s) of surface coating cracking during operation in these test programs were possible. Typically, a substantial degree of surface cracking was observed during posttest examination of Rover/Nerva fuel elements in their upstream, low-to-moderate temperature region, which could have happened in part during cooling of the material at shutdown. An example of this is displayed in Fig. 8, which shows the number of cracks in a Zr–C coolant channel coating as a function of length for a NF–1 composite fuel element.[7,8] These data, which have been examined in great detail in the past, are likely to be of little use to correlate fuel element surface coating cracking during operation because of the high thermal and structural loading experienced by the fuel elements during test reactor shutdown.

B. Nonuniform Loading and Cycling

Another major hydrogen corrosion initiator is nonuniform loading and/or cycling of the fuel material. Nonuniform loading of the fuel material can be induced by mechanical and/or thermal loading means. Mechanical loading of this type can be induced by 1) the presence of preload stresses in the fuel material during assembly or application of a material coating(s) and 2) the presence of nonuniform and/or unsteady pressure (flow) and nonuniform axial temperature distribution(s) during operation. Nonuniform, varying pressure(s) are always present during NTP engine system transient operation conditions. Nonuniform thermal loading conditions are typically present, due to nonuniform axial and radial fission power profiles in the reactor core, when nonuniform/unsteady flow is present, as well as when local core coolant flow and reactor power generation profile(s) are mismatched. Cycling of the fuel material can also introduce residual stresses. For example, heating the material to high temperature during operation may cause it to undergo some degree of creep. When this material cools down, depending on the fuel design configuration, it may experience high compression and large tensile stresses. These conditions can produce high internal material thermal and/or mechanical stresses, which can amplify a stress mismatch between the surface coating and fuel substrate. As previously mentioned, such a condition typically favors cracking of the surface coating. The increase in surface area cracking enhances corrosion and accelerates the mass loss rate. It has also been shown in the Rover program that nonuniform loading and steady-state thermal expansion of the material can help reduce corrosion locally.[7] This process tends to close up surface-coating cracks, hence, retarding corrosion from occurring.

Significant nonuniform and cyclic loading effects were present in the Rover and Nerva program reactors and have contributed, both in a positive and a negative sense, to fuel corrosion.[6,7] Due to the axial flow fuel element design associated with these reactors, substantial mechanical preloading of the elements was required to hold them in place within a tie-tube assembly. This assembly was supported from a plate located at the forward end of the reactor (Fig. 9).[4] Unsteady, channel flows and high thermal gradients were observed in the reactor core because of the nonuniform axial and radial fission power profiles.[4,6] Nonuniform loading and material expansion effects are also considered major contributors for reducing the fuel mass loss rate at the fuel element axial position just downstream of the peak rate (Fig. 1). This is attributed to the

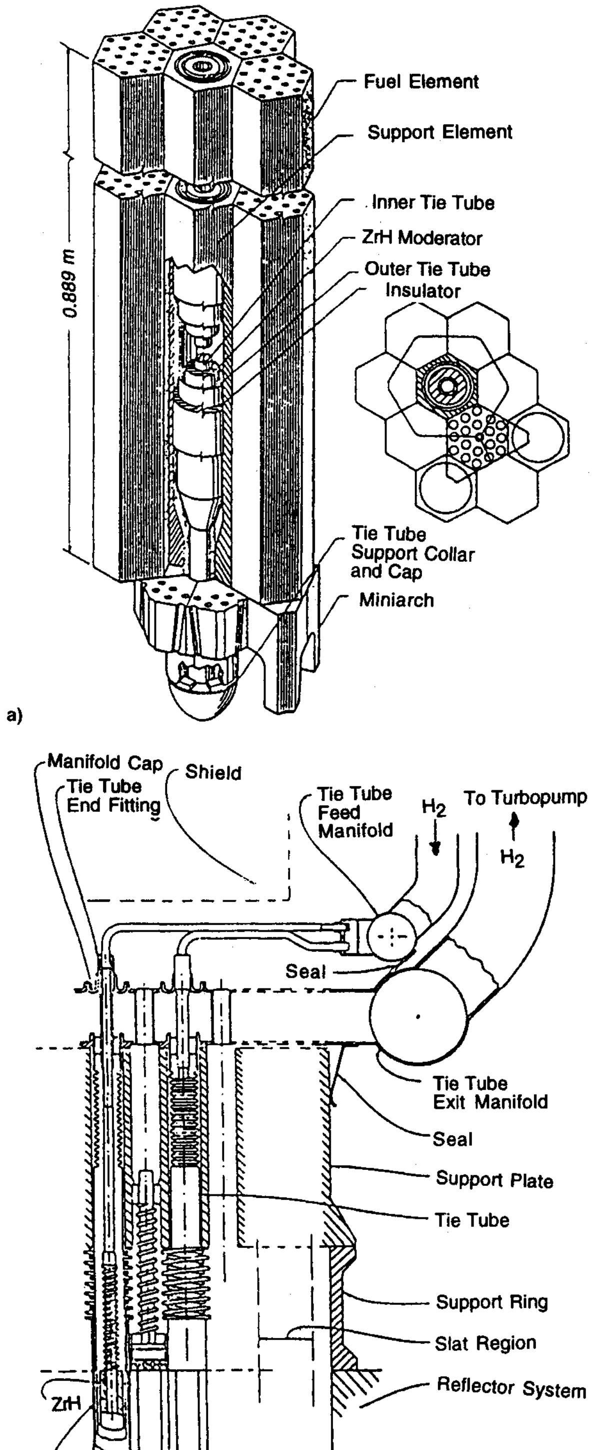


Fig. 9 Typical axial reactor core fuel tie-tube assembly (small space engine example)[4]: a) fuel element support hardware and b) core inlet region design.

closing of a large number of coolant channel surface coating cracks, due to the presence of the nonuniform loading mechanism(s).

C. Radiation Exposure

The exposure of carbide fuel materials to nuclear radiation, expressed in terms of fluence (fluence = $\phi \times t$; where ϕ is the neutron flux and t is the exposure time), and neutron energy spectrum can be major corrosion drivers. If radiation exposure is great enough, material point defects can be produced locally, reducing the thermal conductivity and the ductility of the material. The lower material thermal conductivity and ductility can produce high thermal gradients and cause cracking of fuel coatings and/or the fuel, if uncoated, at the surface. This cracking can increase local corrosion, as previously discussed, which is likely to occur in high neutron flux regions of the NTP reactor. At high local core temperatures it may be possible to heal many of the radiation induced defects by creep and, hence, reduce local corrosion in these high flux regions.

Initially, during the Rover program it was felt that radiation effects on carbide-based fuels, which are high in carbon content, would be minimal, because of the high resistance of carbon to radiation and the short total operation time of an NTP engine system.[8] This was found not to be the case because of the high-power densities in these reactors. Posttest inspection of Rover and Nerva reactor fuel elements has shown that material defects caused by radiation exposure, reduces local material thermal conductivity and ductility, and were considered likely mechanisms to promote cracking.[6–8] The resulted cracking could be correlated to radiation flux profile in the reactor as shown in Fig. 10, but as previously discussed, one must consider the fuel shutdown and fuel operation duty cycle effects in interpreting these data to form such a conclusion. Original interpretation of these observations indicated that the radiation-induced property changes were likely caused by the interaction of fission fragments with the fuel element's graphite lattice.[8] A recent evaluation of the NF-1 test data indicates that radiation embrittlement (a reduction in material ductility) likely occurred.[33] It was concluded from this assessment that radiation embrittlement was likely one of many mechanisms, which also contributed to surface coating cracking.

D. Creep of Material Defects

In reactor regions where high material temperatures are present, healing of material defects is likely due to creep. This competing corrosion process (Fig. 2a) can close surface cracks, as well as reduce material defects internal to the fuel substrate region. Stress relief and physical transport material properties associated with this competing mechanism can help reduce and/or close or inhibit the growth of pre-existing or newly formed surface cracks.[24] Likewise, these phenomena tend to reduce interface stress mismatches between the surface coating and the fuel substrate, and internal fuel substrate stress gradients, which are caused by radiation exposure and/or nonuniform external mechanical and thermal loading. These process features tend to reduce the effective surface area exposed to the hot hydrogen, which in turn inhibits corrosion. Recent analysis of NF-1 test data indicates that the influence of creep can be less than expected when one considers thermal cycling effects.[33]

E. Other Considerations

Many of the physical mechanisms that affect hydrogen corrosion are difficult to characterize due to their inherent complex nature. In addition to the difficulty of understanding these mechanisms at traditional benign conditions, such as those typical of terrestrial power reactor systems, they are magnified at conditions that are characteristic of NTP reactors. Many of these processes, such as material creep and carbon/hydrogen chemical kinetics, e.g., can be influenced by the high radiation fluxes encountered in NTP reactors.[29,32] These effects should also be considered in future corrosion modeling efforts.

As shown in Fig. 2a, the hydrogen corrosion reaction process branch is the only process path where carbide material mass loss occurs. The mass loss from this process path will likely weaken the materials lattice structure, and hence, will further contribute to the fuel material mass loss rate by erosion. This fuel mass loss process path is not shown in Fig. 2a because it was not considered as a fundamental process mechanism that directly influences the corrosion process. It should be noted that it may be possible for fuel erosion to indirectly influence corrosion by affecting the surface area exposed to hydrogen.

Creep and high-temperature annealing of high carbide content materials at high temperatures are believed to be major contributing factors that provide a likely explanation on why fuel mass loss observations were typically lower than that expected at the downstream, high-temperature location of Rover/Nerva fuel elements, as shown in Fig. 1.[4,6–8] Other corrosion-inhibiting processes, which support mass loss observations in the development reactor tests, are the presence of hydrocarbon species in the hydrogen coolant gas in the downstream fuel element region, as previously discussed. These hydrocarbons are produced in the low-to-moderate temperature, radiation exposure region and are carried away by the upstream flow and deposited on the surface of the fuel material in the downstream fuel element region. Because of the cosine axial fission power generation profile typical of these reactors, the fuel temperature peaks slightly above the core midplane (Fig. 10). Therefore, it is expected that the corrosion rate will be the highest in the lower half of the reactor core. These results suggest that flattening the fission power profiles in the reactor core could help reduce the material mass loss.

By understanding the many competing physical processes associated with hydrogen corrosion of carbide materials, one may be able to interpret the fuel mass loss profiles and corresponding observations at conditions typical of past Rover and Nerva reactor tests (Fig. 1). Such understanding will also provide qualitative engineering insight into the potential of corrosion occurring and its impact on future NTP carbide fuel reactor designs. Dominant hydrogen corrosion processes typical of carbide fuel solid-core reactors employing either axial or radial flow designs are shown in Fig. 11. Due to their dissimilar flow paths and corresponding temperature profiles, the dominant hydrogen corrosion mechanisms in these solid-core concepts could be quite different.

One must also consider the numerous interrelated corrosion mechanisms on a smaller scale. The orderly (predictable) channel flow characteristics and past experience base of axial flow geometries establishes a basis to begin corrosion prediction modeling of more complex radial flow packed particle bed reactor configurations. The complexity and the highly turbulent nature of the flowfield in the packed particle bed reactors and the higher surface area-to-volume ratio of the fuel core design (microspheres or pellets) can greatly affect its corrosion characteristics and rate.

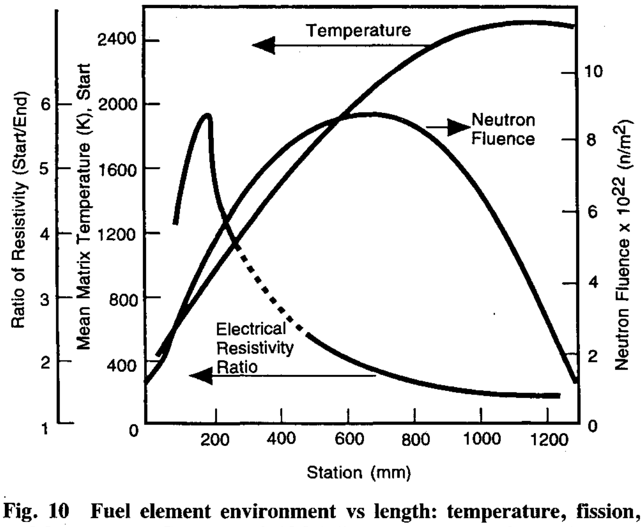
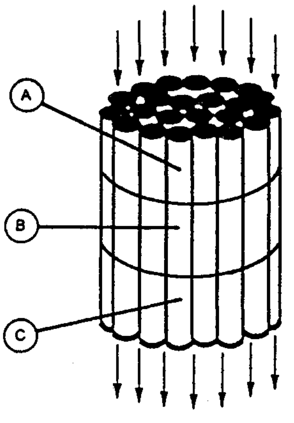
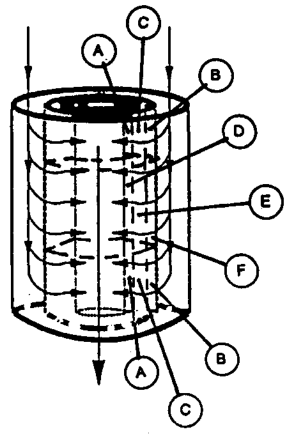


Fig. 10 Fuel element environment vs length: temperature, fission, and fast neutron fluence (>0.18 MeV), as well as the change in room temperature electrical resistivity ratio for a NF–1 test composite fuel element from pre- and posttest observations.[8]



REGION	PROCESS MECHANISM
A	Non-uniform Loading, Thermochemistry
B	Radiation, Thermochemistry
C	Vaporization, Creep

a)



REGION	PROCESS MECHANISM
A	Vaporization, Creep
B	Thermochemistry
C	Non-uniform Loading, Thermochemisty
D	Radiation, Vaporization, Creep
E	Radiation, Thermochemistry
F	Radiation, Non-uniform Loading, Thermochemistry

b)

Fig. 11 Dominant corrosion process mechanisms associated with various regions of a) axial and b) radial flow reactor cores.

III. Corrosion Modeling and Future Requirements

Previous discussion has shown that hydrogen corrosion of carbide fuel materials is complex and can be influenced by numerous fuel design and reactor operation parameters. Past modeling efforts have focused only on the thermochemical aspects of this process.[14,15,31] No modeling effort to date has been accomplished that integrates the other interrelated physical processes discussed earlier. Development of such an inclusive corrosion model presents many challenges in terms of accurately quantifying the various complex processes, coupling them appropriately, and benchmarking the model predictions. The following discussion addresses corrosion modeling issues and considerations that were identified during this review, and the impact of developing such a robust, accurate model based on fundamental physical principles to support the developments of future NTP engine systems.

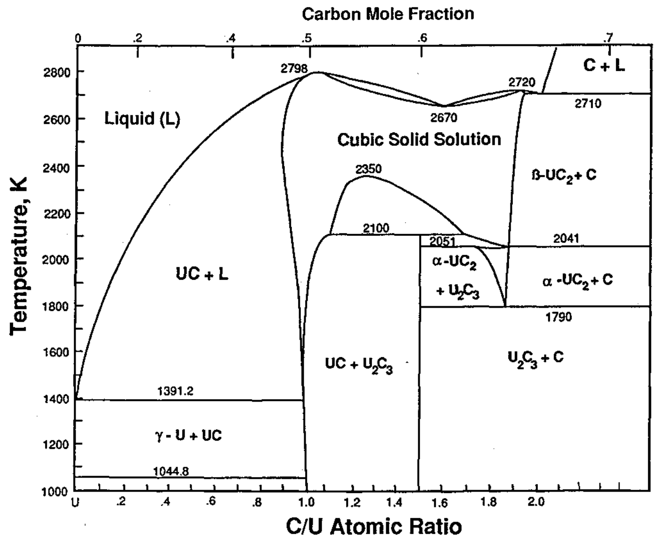


Fig. 12 U–C binary phase diagram.[30]

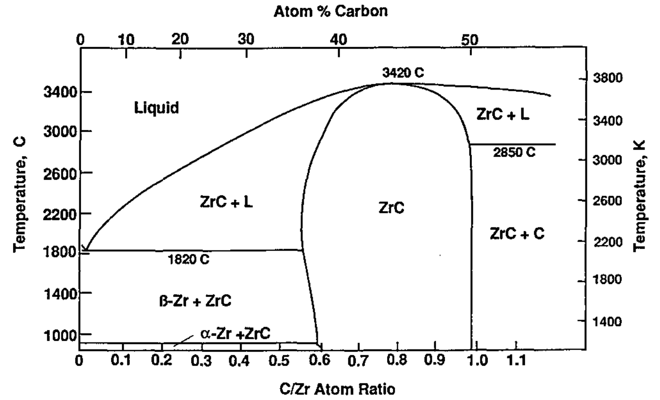


Fig. 13 Zr–C binary phase diagram.[14]

Table 1 Possible corrosion model reaction mechanisms

Transport controlled	Surface reaction rate controlled
Diffusion of reactant gas species from the gas stream to the solid surface through a solid, liquid, or gaseous boundary layer Diffusion of product gas species from the solid surface to the gas stream through a solid, liquid, or gaseous boundary layer	Adsorption of the reactant gas species on the solid surface Desorption of the product gas species from the solid surface to the gas stream or boundary layer Surface diffusion of adsorbed gas species on the solid surface to achieve sites for reaction or to sites where other adsorbed species are present, the combination of which can induce a reaction (e.g., a localized catalysis event) Cracking or dissociation of gas species to more reactive forms

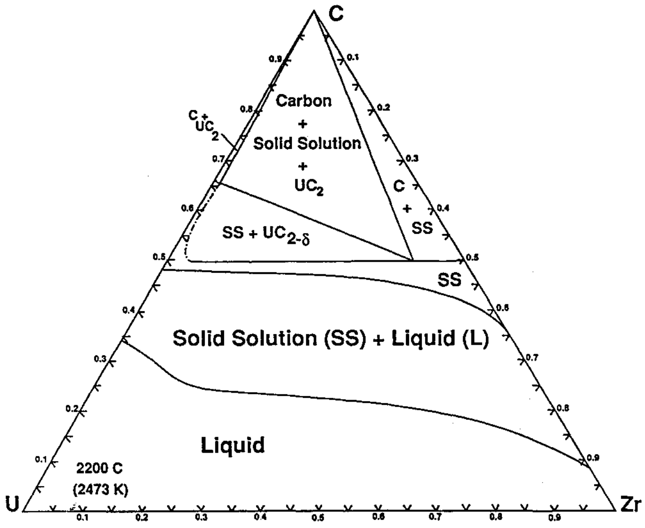


Fig. 14 Isothermal ternary phase diagram for the U–Zr–C material system at 2473 K.[27]

In order to model the vaporization behavior of refractory carbide fuels, it is necessary to know the equilibrium partial pressures of the important vapor species. When, e.g., a $U_xZr_{1-x}C_y$ fuel is undergoing hydrogen corrosion, the most important vapor products are U, Zr, and hydrocarbons. Initially, these gaseous products leave the fuel surface at different rates. Because this solid solution exhibits a wide range of stoichiometry, the fuel composition can change significantly during vaporization or corrosion. Any change in composition will affect the equilibrium vapor pressures. Figures 12 and 13 show the binary phase diagrams for the U–C and Zr–C systems, respectively; whereas Fig. 14 displays an isothermal ternary phase diagram for the U–Zr–C system at 2473 K. For all of the carbide material systems shown, the physical phase states are highly dependent on its chemical composition and stoichiometry.

To be able to model the vaporization or corrosion of a gas/solid reaction a priori, it is necessary to know specifically the rate-controlling mechanism or mechanisms. Mass loss may be transport controlled, reaction-rate controlled, or may be caused by a combination of two or more mechanisms. Table 1 lists many of the possible reaction mechanisms one must consider in developing a corrosion model.

Two models were developed that describe the corrosion kinetics of solid-solution $U_xZr_{1-x}C_y$ nuclear fuel materials in hydrogen gas at 1 atm, in the range of 2500–3000 K.[14,15] Both models suggest that the corrosion is controlled by vapor transport. In the later model, it was found that the corrosion of $U_xZr_{1-x}C_y$ is rate limited by the gaseous transport of Zr(g) away from the solid surface through a gaseous boundary layer where the partial pressure of Zr(g) at the surface is determined by the congruently vaporizing surface composition.[15] Recent modeling work also addresses the effectiveness of carbide coating on graphite to impede hydrogen corrosion.[31]

Based on the extensive review of available literature performed recently in the areas of corrosion of NTP reactor fuel materials, modeling, supporting experimental databases and related reactor design practices and technologies, a number of major outstanding technical issues have been identified:

1) The lack of qualitative (integrated) understanding of radiation, preloads/nonuniform loading, creep, and flow structure effects on the overall corrosion processes.

2) The lack of single-effects data for the various competing corrosion processes at realistic NTP engine system operating conditions.

3) The validity and/or scaling of nonnuclear testing for material compatibility testing.

These issues must be addressed to support the initial development of an accurate corrosion model. To address these issues, a modest, sustained research investment will be required to develop fundamental understanding and a supporting experimental database. The following discussion provides the rationale in the selection of these outstanding issues.

Current carbide corrosion models lack an integrated approach to quantify the effects of the different corrosion mechanisms such as exposure to nuclear radiation, preload/nonuniform loading, annealing, and flow structure effects. Instead, modeling of hydrogen corrosion has focused on thermochemical corrosion mechanisms, as previously mentioned. Although thermochemical processes are important, other competing corrosion mechanisms, previously discussed, are also major contributors to hydrogen corrosion and mass loss of NTP reactor materials. This fact was confirmed by detailed posttest examination of Rover and Nerva reactor fuel elements.[4,6–8] The importance of all of the competing corrosion processes was recognized by the reactor scientific team that supported the fuel and reactor design developments. Even with this knowledge no multiprocess modeling of the hydrogen corrosion phenomena has been attempted to date. Hence, the current corrosion-modeling capabilities need to be revised to include many of the physical processes identified, ideally to at least a first-principle level basis. Sensitivity studies should then be performed to provide the necessary insight into the coupling of the various competing corrosion mechanisms. Results from such studies will also be useful in identifying the critical tests required to supply the benchmark data necessary to properly verify the modeling approach and assumptions.

Another key issue is the lack of fundamental single-effects data associated with the various corrosion mechanisms expected at typical NTP operation conditions.[13] Such data are required to support both modeling development and verification activities. As previously mentioned, the availability of such data is limited and is at best marginal, due to the disparity between the test conditions and those typical of NTP reactors. The importance of having these fundamental data cannot be overemphasized.

The third and last major outstanding technical issue identified addresses the value of nonnuclear carbide material/hydrogen compatibility testing. This issue could have a major potential impact on material compatibility testing complexity and cost. A review of past Rover and Nerva data indicated that radiation damage does affect hydrogen corrosion.[4,6–8] Additionally, it was the consensus of a forum of international technical specialists in this area that the question of nuclear vs nonnuclear material compatibility testing is still an important, open-ended issue.[34] They also stated that even if nonnuclear material compatibility tests are considered valid, the method of heating the test sample, typically induction or ohmic heating, has produced conflicting results in the past. More discussion of the modeling technical issues and their potential interrelationship to future NTP reactor fuels corrosion modeling and system development effort(s) are provided in Ref. 35.

IV. Concluding Remarks

Hydrogen corrosion of carbide fuel materials in NTP systems greatly impacts the engine performance, thrust-to-weight, and operation life, and is considered by many to be a critical development issue. Experience from the Rover and Nerva programs has shown the effects of corrosion to be substantial and highly complex. Hydrogen corrosion phenomena are driven by many highly coupled and interrelated physical processes. These processes include 1) exposure to hot hydrogen that produces thermochemical reactions of various types, 2) preload and nonuniform heating and mechanical loading, 3) exposure to nuclear radiation, and 4) high-temperature creep. Coatings have been used in the past to combat corrosion, but only moderate success has been achieved. This level of success can be attributed to the complex nature and the degree of (or lack of) understanding of the many interrelated fuel design and operation factors and their influence on corrosion.

Using the past Rover and Nerva experience base as a guide, major interrelated physical process mechanisms were identified and discussed that characterize the current understanding of hydrogen corrosion of candidate high-temperature NTP carbide fuel materials. Due to the lack of hydrogen/carbide material compatability test data and modeling capability, future efforts should focus on 1) developing a corrosion model that couples all major interrelated physical process mechanisms, even if they are only included on a first-principle level basis, 2) acquiring fundamental single-effect(s) data at realistic NTP reactor operational conditions, and 3) determining the validity of nonnuclear experimental results to the characterization of carbide material compatibility with hydrogen in NTP reactors. Additionally, a dedicated effort should also be undertaken to capture the vast experience of the U.S.S.R. in this area, and integrate it with the U.S. knowledge base.

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References

[1] Bussard, R. W., and DeLauer, R. D., *Fundamentals of Nuclear Flight*, McGraw–Hill, New York, 1965.

[2] Borowski, S. K., Clark, J. S., McIlwain, M. C., and Pelaccio, D. G., "Nuclear Thermal Rockets: Key to Moon-Mars Exploration," *Aerospace America*, Vol. 30, No. 6, 1992, pp. 34–37.

[3] "America at the Threshold-America's Space Exploration Initiative," Rept. of the Synthesis Group, Superintendent of Documents, U.S. Government Printing Office, Washington, DC, June 1991.

[4] Koenig, D. R., "Experience Gained from the Space Nuclear Rocket Program (Rover)," Los Alamos National Lab., Rept. LA-10062-H, Los Alamos, NM, May 1986.

[5] Clark, J. S. (ed.), *Proceedings of the NASA/DOE/DOD Nuclear Thermal Propulsion Workshop* (Cleveland, OH), 1990 (NASA-10079).

[6] Finseth, J. L., "Rover Nuclear Rocket Engine Programs; Overview of Rover Engine Tests—Final Report," NASA Contract NAS 8-37814, Feb. 1991.

[7] Taub, J. M., "A Review of Fuel Element Development for Nuclear Rocket Engines," Los Alamos Scientific Lab., Rept. LA-5931, Los Alamos, NM, June 1975.

[8] Lyon, L. L., "Performance of (U,Zr)C-Graphite (Composite) and of (U,Zr)C (Carbide) Fuel Elements in the Nuclear Furnace 1 Test Reactor," Los Alamos Scientific Lab., Rept. LA-5398-MS, Los Alamos, NM, Sept. 1973.

[9] Matthews, R., Blair, H., Chidester, K., and Davidson, K., "Carbide Fuels for Nuclear Thermal Propulsion," AIAA Paper 91-3455, Sept. 1991.

[10] Carmack, W. J., Hobbins, R. R., and Lessing, P. A., "Mixed Carbide High-Temperature Fuels," AIAA Paper 91-3453, Sept. 1991.

[11] Homan, F. J., Napier, J. M., and Caldwell, C. S., "Particle Fuels Technology for Nuclear Thermal Propulsion," AIAA Paper 91-3457, Sept. 1991.

[12] Storms, E. K., Hanson, D., Kirk, W., and Goldman, P., "Effect of Fuel Geometry on the Life Time-Temperature Performance of Advanced Nuclear Propulsion Reactors," AIAA Paper 91-3454, Sept. 1991.

[13] Pelaccio, D. G., El-Genk, M. S., and Butt, D. P., "A Review of Carbide Fuel Corrosion for Nuclear Thermal Propulsion Applications," *Proceedings of the 11th Symposium on Space Nuclear Power and Propulsion Systems*, edited by M. S. El-Genk and M. D. Hoover, AIP 301, Vol. 2, American Inst. of Physics, New York, 1994, pp. 905–918 (CONF-940101).

[14] Storms, E. K., "The Behavior of ZrC_{1-x} and $U_yZr_{1-y}C_{1-x}$ in Flowing Hydrogen at Very High-Temperatures," Los Alamos National Lab., Rept. LA-12043-MS, Los Alamos, NM, Jan. 1992.

[15] Butt, D. P., "Corrosion of $U_xZr_{1-x}C_{1-y}$ Nuclear Fuel Materials in Hydrogen Gas at High Pressures and Temperatures," International Astronautical Federation Paper 92-0570, Aug.–Sept. 1992.

[16] MacMillan, D. P., "Overview of Fuel Element Development and Mass Loss Rate Experiments on Uranium-Zirconium Carbide Fuel," *Proceedings of the 8th Symposium on Space Nuclear Power Systems*, edited by M. S. El-Genk and M. D. Hoover, AIP 217, Vol. 3, American Inst. of Physics, New York, 1991, pp. 1037–1044 (CONF-910116).

[17] Krakowski, R. A., and Olander, D. R., "Survey of the Literature on the Carbon-Hydrogen System," Univ. of California Lawerence

Radiation Lab., Rept. UCRL-19149, Berkeley, CA, 1968.

[18]Chi, J. W. H., and Landahl, C. E., "Hydrogen Reactions with Graphite Materials at High-Temperatures and Pressures," *Nuclear Applications*, Vol. 4, March 1968, pp. 159–169.

[19]Chi, J. W. H., "Hydrogen Corrosion of Graphite Materials and Graphite Reactor Components," Westinghouse Astronautics Lab., Rept. WANL-TME-1151, Pittsburgh, PA, 1965.

[20]Burghardt, R. R., "Corrosion Inhibitor Tests," Westinghouse Astronautics Lab., Rept. WANL-TME-1298, Pittsburgh, PA, Sept. 1965.

[21]Rodgers, J. D., and Sesonske, A., "Analysis of Graphite-Hydrogen-Methane Kinetics Above 1600 K," *Nuclear Technology*, Vol. 73, May 1986, pp. 236–242.

[22]Sanders, W. A., "Rates of Hydrogen-Graphite Between 1550° and 2260°C," NASA Rept. TN D-2738, Jan. 1965.

[23]Clarke, J. T., and Fox, B. R., "Reaction of Graphite Filaments with Hydrogen Above 2000°K," *Journal of Chemical Physics*, Vol. 46, No. 3, 1967, pp. 827–836.

[24]Connell, L. W., "Hydrogen Corrosion of Graphite Nozzles for a Particle Bed Nuclear Rocket," Sandia National Lab., SAND 89-0004, Albuquerque, NM, Nov. 1989.

[25]Botts, T. E., Horn, F. L., Jones, O. C., Lazareth, O. W., Ludewig, H., Powell, J. R., and Usher, J. L., "The Rotating and Fixed Bed Reactor Concepts," Brookhaven National Lab., Air Force Rocket Propulsion Lab., TR 83-023, Upton, NY, Nov. 1983.

[26]El-Genk, M. S., Morley, N. J., Pelaccio, D. G., and Juhasz, A., "Pellet Bed Reactor Concepts for Nuclear Propulsion Applications," *Journal of Propulsion and Power*, Vol. 10, No. 6, 1994, pp. 817–827.

[27]Clark, J. S., McDaniel, P., Howe, S., Helms, I., and Stanley, M., "Nuclear Thermal Propulsion Technology: Results of an Interagency Panel in FY 1991," NASA TM-105711, April 1993.

[28]Butt, D. P., and Wallace, T. C., "The U-Zr-C Ternary Phase Diagram Above 2473 K," *Journal of the American Ceramic Society*, Vol. 79, No. 6, 1993, pp. 1409–1419.

[29]Olander, D. R., "Fundamental Aspects of Nuclear Reactor Fuel Elements," Dept. of Energy, Rept. TID-26711-P1, 1976.

[30]Matthews, R. B., Baars, R. E., Blair, H. T., Butt, D. P., Mason, R. E., Stark, W. A., Storms, E. K., and Wallace, T. C., "Fuels for Space Nuclear Power and Propulsion: 1983–1993," *A Critical Review of SPACE NUCLEAR POWER AND PROPULSION 1984–1993*, edited by M. S. El-Genk, American Inst. of Physics, New York, 1994, pp. 179–220.

[31]Wallace, T. C., and Butt, D. P., "Diffusion and Vaporization of Transition Metal Carbides as It Relates to Diffusion Coupled Vaporization Processes: A Review," Los Alamos National Lab., Rept. LA-UR-93-2903, Los Alamos, NM, 1994.

[32]Nightingale, R. E. (ed.), *Nuclear Graphite*, Academic, New York, 1962.

[33]Dhalla, A. K., Hundal, R., and Brengle, R., "NERVA/Rover Fuel Element Midband Corrosion Analytical Evaluation of the Possible Mechanisms for Loss of Coating Integrity," *Proceedings of the 11th Symposium on Space Nuclear Power and Propulsion Systems*, edited by M. S. El-Genk and M. D. Hoover, AIP 301, Vol. 2, American Inst. of Physics, New York, 1994, pp. 931–938 (CONF-940101).

[34]El-Genk, M. S., and Pelaccio, D. G. (eds.), *Proceedings of the Workshop on Hydrogen Corrosion in Nuclear Thermal Propulsion Reactors*, 10th Symposium on Space Nuclear Power and Propulsion (Albuquerque, NM), 1994, p. 198.

[35]Pelaccio, D. G., and El-Genk, M. S., "A Review of Nuclear Thermal Propulsion Carbide Fuel Corrosion and Key Issues—Final Report," NASA Grant NAG3-1346, Nov. 1994.