

Investigation of Refractory Carbide Behavior in Flowing Hydrogen at Very High Temperatures Relevant for Nuclear Thermal Propulsion Applications

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DEDICATION

This work is dedicated to my parents, Lorraine and Matthew, who have always loved, supported, and believed in me.

To my siblings, Andrew, Josephine, and Philip, who I will always love, support, and believe in.

To Raul, who has shown me how to thrive in both my career and life.

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ABSTRACT

Nuclear thermal propulsion (NTP) is an in-space propulsion technology capable of high specific impulse (850 – 1100 s) and thrust (10 – 250 klbf). Due to their high melting temperature and favorable nuclear properties, refractory carbides (RCs) are attractive matrix candidates for NTP applications. In this thesis, the performance of SiC, TiC, and ZrC in NTP relevant environments (high temperature, flowing hydrogen) was investigated through thermodynamic modelling and hot hydrogen testing. Intrinsic RC compatibility with hot hydrogen was investigated through testing of high purity sample coupons in unpressurized, flowing hydrogen at relevant temperatures (2000 – 2500 K) and time scales (<120 minutes). Nano-infiltrated transient eutectic (NITE) SiC samples were tested to identify deviations in corrosion behavior due to relevant manufacture parameters required for fabrication.

Thermodynamic calculations predicted ZrC to be most stable, followed by TiC, and SiC. Experimental observations confirmed this trend and active attack of all materials observed. SiC exhibited acceptable hydrogen compatibility up to 2150 K. NITE SiC exhibited greater weight loss than pure SiC, due to preferential attack of sintering additives (Al_2O_3 and Y_2O_3). High purity TiC and ZrC coupons exhibited acceptable hydrogen compatibility for all temperatures. Use of SiC, produced with current NITE manufacture technology, as a fuel matrix should be limited to temperatures below 2250 K due to high temperature incompatibility of sintering aids and the matrix. Identification of alternative sintering aids capable of higher temperature compatibility or development of TiC or ZrC matrices derivative of current manufacture technologies can enable higher performing NTP systems.

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CHAPTER ONE - INTRODUCTION AND MOTIVATION

Background

Since the 1950s, nuclear technologies have been developed for space exploration in and beyond low earth orbit (LEO). Due to high power density provided by nuclear reactions, these systems can provide high power levels for long periods of time in deep space compared to alternative energy sources (figure 1.1). Nuclear thermal propulsion (NTP) is an in-space propulsion technology capable of providing high thrust (10 – 250 klbf) and specific impulse (850 – 1100 s). NTP has been extensively developed in the United States and former Soviet Union through various programs spanning from the 1950s up to the present. The most significant U.S. development efforts were incurred during the nuclear engine for rocket vehicle application (NERVA)/Rover program, which included extensive engine/reactor development and testing with over 20 prototype reactors built and ground tested spanning 1955 – 1972 [1, 2].

Nuclear thermal rockets (NTRs) function similarly to chemical engines, in that a propellant is heated to extremely high temperature and expanded out a nozzle to provide thrust. However, instead of heating the propellant via combustion reaction, NTRs utilize a nuclear reactor as a heat exchanger to transfer the energy generated from fission to heat the propellant to very high temperatures (> 2350 K). Through the use of a low molecular mass propellant, typically hydrogen (H_2), NTP is capable of specific impulse (I_{sp}) values of nearly twice that of the highest performing chemical engines (~ 450 s). The combination of high thrust and I_{sp} permits faster trip times and increased flexibility for crewed missions to destinations beyond LEO. This is especially desirable for crewed missions as reduced trip time minimizes astronauts' exposure to harmful physical health effects due to microgravity and space radiation, as well as deleterious psychological effects stemming from long term confinement during transit [3].

While historic NTP programs have established the overall feasibility of a working NTP system. There still exist challenges to implementing NTP technologies as a competitive in-space propulsion alternative for future missions. These challenges include improving the overall technology readiness level (TRL) by overcoming unresolved development challenges and establishing the infrastructure needed for rigorous testing and development as a part of the qualification process of the system. Historic NTP engine designs have been optimized to meet past performance needs by minimizing engine (reactor) sizes for a given thrust level using high-enriched uranium (HEU) fuel and a fast or epithermal reactor spectrum. However, recent studies

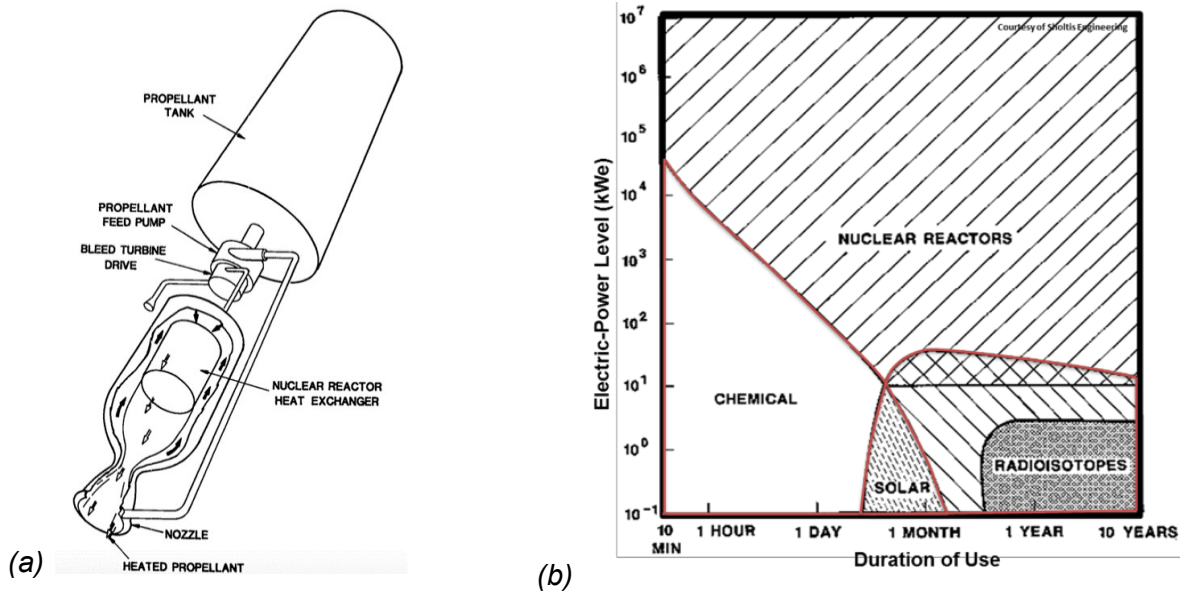


Figure 1.1 (a) Nuclear thermal propulsion propellant flow path diagram. Propellant acts to provide cooling of the reactor core/rocket structural components and thrust when expanded through the nozzle [1]. (b) Energy density of various power sources in space. Nuclear power sources provide the potential for use of high power for long time periods [14].

have shown that low enriched uranium (LEU) engine designs containing less than 20 wt% ^{235}U content, are capable of achieving comparable performance to HEU engine designs if the neutron spectrum is moderated to allow for more thermal fissions [4-13]. Use of LEU fuel has the potential to reduce the high facility maintenance cost and perceived political hurdles of developing NTP systems traditionally associated HEU fuel systems. Further, LEU NTR engine designs can promote future development and licensing of NTRs for private industry. Other recent NTP developments have shown that the utilization of modern manufacturing technologies and design techniques, such as spark plasma sintering (SPS), can be leveraged to facilitate the manufacture of more desirable microstructures or enable manufacture of new classes of material systems, which may be specifically advantageous for use in a LEU NTR engine.

The purpose of the research pursued under this thesis is to investigate the behavior of refractory carbides (RCs): silicon carbide (SiC), titanium carbide (TiC), and zirconium carbide (ZrC) as novel structural matrix candidates for LEU NTP applications. The following sections in this introduction overview a background of in-space propulsion performance metrics necessary for competitive NTP performance, derived NTP operating parameters and materials needs within the NTR, as well as a summary historic fuel development for NTP applications. A description of design philosophy and attributes of RC-matrix fuel systems for NTP applications is discussed and major research objectives of this thesis introduced.

Performance Parameters for In-Space Propulsion Methods

When considering in-space propulsion methods for crewed interplanetary missions, the most effective propulsion methods reduce transit times, increase available cargo mass, and are cost effective (high perceived development status) [15]. As previously overviewed, reduced trip times minimize cosmic radiation doses, psychological effects from prolonged confinement, and physical effects of microgravity to the crew in space. Additionally, reduced trip times can enable more flexible trajectory paths to be considered during mission planning, thereby allowing for longer surface stays, more flexible launch windows, or abort windows for the same overall mission duration [16]. Ultimately, the less time spent in space during transit allows for safer crewed missions and longer surface stays, resulting in greater science payoff for the economic and technological investment for crewed missions. Current methods of chemical propulsion require trip times of over six months to reach mars and require surface stays of either only 30 days or more than 500 days based on identified near term trajectories [17]. To reduce trip time and increase available cargo mass, alternative in-space propulsion methods must demonstrate increased efficiency (specific impulse) and the capability to enable quick accelerations to meet the velocity requirements to satisfy available trajectories (thrust).

Specific impulse (I_{sp}) is a measure of the efficiency of different propulsion methods and is determined by the ratio of thrust to the propellant mass flow through the engine (equation 1.1):

$$I_{sp} = \frac{F_{thrust}}{\dot{m}} = \frac{1}{g_0} \sqrt{\left[\frac{2\gamma}{\gamma - 1} \frac{RT}{M} \right] \left[1 - \frac{p_e}{p_c} \right]^{\frac{\gamma-1}{\gamma}}} \propto \sqrt{\frac{T}{M}} \quad (\text{Eq. 1.1})$$

F_{thrust} – thrust (force)

$\dot{m}$ – mass flow rate

g_0 – gravitational constant

γ – constant volume specific heat

R – ideal gas constant

M – molecular mass

T – propellant exit temperature. p_e – propellant exit pressure p_c – chamber pressure

I_{sp} compares how much propellant is necessary to provide a desired thrust for different propulsion methods. Thrust is the forward force that accelerates a rocket in space. Engines with higher specific impulse values require less propellant mass to reach a destination (Equation 1.2):

$$F_{\text{thrust}} = v \frac{dm}{dt} \approx v_e \dot{m} \quad (\text{Eq. 1.2})$$

F_{thru} – thrust (force) v_e – propellant exit velocity $\dot{m}$ – propellant mass flow rate

Reducing the necessary propellant for a system is the most efficient way to cut down on the entire mass of the mission architecture. Typical chemical engine designs may designate up to 85% of the total system mass to propellant, while only 15% is designated for structure and payload [18, 19]. Therefore, for the same operating thrust level, doubling the I_{sp} of a rocket decreases the entire mass of the system by nearly half. A combination of high thrust and I_{sp} can enable shorter trip times by reducing the mass of the propellant and increasing the possible acceleration to change the mission velocity increment (Δv) of the rocket (Equation 1.3):

$$\Delta v = \int_{t_0}^{t_1} \frac{F_{\text{thrust}}(t)}{m(t)} dt \approx v_e \ln \left(\frac{m_0}{m_1} \right) \quad (\text{Eq. 1.3})$$

F_{thrus} – thrust (force) v_e – propellant exit velocity $\dot{m}$ – propellant mass flow rate

High Δv also allows for increased mission flexibility by allowing for alternative trajectories and larger launch, abort windows [6, 7, 20].

As derived from Eq. 1.1, I_{sp} is maximized when propellant molecular mass is minimized and propellant outlet temperature is maximized, thus driving typical NTP reactor designs with ultra-high proposed operating temperatures (> 2350 K) and use of a low molecular mass H_2 propellant. The highest performing chemical engines are capable of ~ 450 s of specific impulse with the combustion of liquid hydrogen and liquid oxygen fuel (H_2O propellant after reaction), while NTP systems are capable of providing comparable thrust and high I_{sp} (850 – 1100 s) with the use of a hydrogen propellant and operating temperatures in excess of 2350 K, as shown in figure 1.2. Since nuclear rockets enable thrust levels comparable to chemical engines with complementary high specific impulse, trip times to Mars are expected to be up to half of that of the best current in-space chemical propulsion methods.

Other variants of nuclear fission power in space include nuclear electric propulsion (NEP). In electric propulsion (EP) systems, such as NEP and solar EP (SEP), a power conversion unit can be integrated with a heat source, such as a nuclear reactor, to provide electric power to a system.

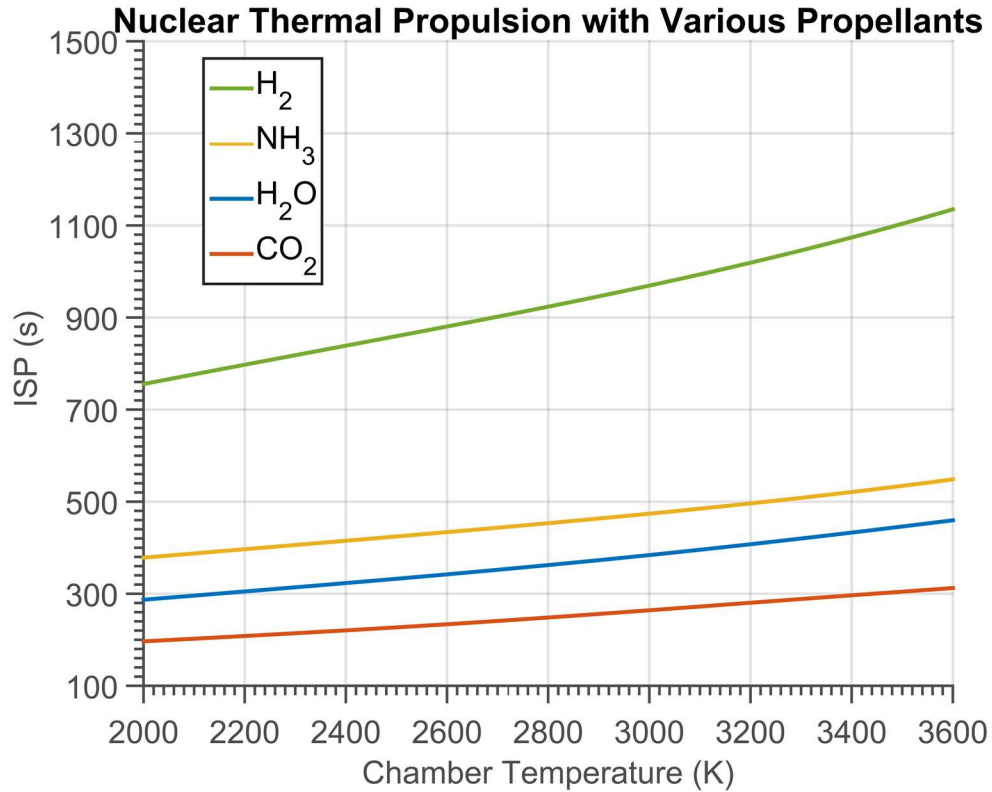


Figure 1.2 Calculated specific impulse of in-space propulsion systems with various propellants. Specific impulse is inversely proportional to the square root propellant mass and directly proportional to reactor outlet (propellant exit) temperature. With a hydrogen propellant, approximately twice the specific impulse of the most efficient chemical engines (H₂O propellant) can be achieved [22].

In order to generate thrust, the electricity can power ion, magnetohydrodynamic (MHD), or variable specific impulse thrusters for propulsion. EP permits very high specific impulse values at the cost of generally much lower thrust levels (table 1.1). Lower thrust levels are typically not desired for crewed missions because they do not enable fast acceleration of the rocket, which may limit desirable trajectories for fast travel. Due to longer operation times required for low thrust propulsion methods, NEP reactor systems are closed systems requiring longer operation lifetimes (higher burnup) and less demanding operating temperatures (800 – 1200 °C) [21]. Other variants of nuclear power for in space propulsion also include radioisotope sources and nuclear fusion. Similar to NEP systems, a radioisotope, instead of a nuclear reactor, is utilized as a heat source to provide electric power in space. Radioisotope thermoelectric generators (RTGs) are a form of electric propulsion. Nuclear fusion encompasses fusion electric propulsion and fusion thermal propulsion, as shown in table 1.1. While NTP encompasses solid, liquid, and gas core configurations, of which each are distinguished by the operating state of the fuel. Solid core nuclear thermal rockets do not allow any melting of the nuclear fuel during operation and correspond to the largest database of fuel development. Thus, these fuels are thought to offer the most straightforward pathway for licensing.

Table 1.1. Performance parameter comparison of various in-space propulsion methods [15].

Type of Propulsion	Specific Impulse (s)	Thrust (klbf)	Propellant	Time of Single Burn (s)	TRL
Chemical (SSME)	452	471	LH ₂ + LO ₂	10 ³	9
Nuclear Thermal Propulsion (solid core)	800 - 1100	25 - 250	H ₂	10 ³	4
Nuclear Electric Propulsion (*xenon ion thruster)	6,000 – 8,500	10 ⁻³ – 10 ⁻¹	Xe Ion	10 ⁷	5*
Nuclear Thermal Propulsion (liquid/vapor core)	1870/300	10 ⁴ /10 ⁵	H ₂	10 ³	3
Fusion Thermal Propulsion	10,000 – 100,000	4 - 10 ²	H ₂	10 ³	2

Materials Needs for Nuclear Thermal Propulsion

In a nuclear rocket, the nuclear reactor acts a heat exchanger to heat a working fluid, the propellant, to extremely high temperatures (typically 2350 – 3000+ K). During each discrete interval of operation, or burn, the propellant is exhausted through a nozzle to provide a force to drive the acceleration of the system. For round trip crewed interplanetary missions, at least four burns are required to accelerate to the destination, to inject into orbit around the destination, as well as to return to earth. Typical reference values for crewed mars missions include single burn times on the order of 5 – 45 minutes, with total operation times of as little as 30 minutes up to 102 minutes based on chosen trajectories [15]. This corresponds to very short operating lifetimes of the reactor compared to terrestrial reactor systems, in a unique operating environment (high temperature, pressurized hydrogen).

Material systems proposed for use must allow for operating temperatures in excess of 2350 K and resist interaction with the corrosive hydrogen propellant in order to enable the high performance desired for in-space propulsion. Due to the dependence of core power (and mechanical loading profiles) on geometry, composition, and mass of reactor components, it is desired to identify materials capable of retaining strength and structural stability, while resisting mass loss, dimensional instability, and/or formation of undesirable phases for the range of operating conditions during the rocket lifetime. High operating temperatures may result in excessive erosion (due to surface vaporization or chemical reactions with the flowing hydrogen) and high thermal stresses between the fuel matrix and relevant interfaces such as protective claddings, coatings, or dispersed fuel particles. Fabricated components must be able to survive thermal shock incurred during start up for a single burn and recover from previous use to maintain performance during multiple restarts of the engine. Therefore, key attributes of material systems for NTP applications should enable:

- *High operating temperature: high melting temperature, low vaporization, thermodynamic stability*
- *Criticality: low thermal neutron absorption, good moderating power*
- *Chemical compatibility with coolant, fuel particles, and relevant component interfaces/claddings up to high temperatures*
- *Mechanical/structural stability over a wide range of operating temperatures: predictable mechanical properties to accommodate thermal stresses, creep, or changes in physical properties with temperature, irradiation*

- *Compositional stability over a wide range of operating temperatures: predictable evolution in material composition under enhanced diffusion expected during irradiation and high temperature operation, no formation of low melting temperature compounds, no migration of dispersed ceramic fuel particles (in the case of fuel system materials)*

Historic Fuel Systems for Nuclear Thermal Propulsion

Several fuel system types have undergone extensive development through historic NTP programs within the United States and Russia. Of these, three major families of structural fuel systems can be categorized: composite graphite matrix fuels, ceramic-metallic (cermet) refractory metal matrix fuels, all-carbide solid solution uranium carbide (UC) based fuels. Each of these fuel systems offer different attributes and limitations, which may be particularly suited for different engine design needs (table 1.2). In this section, known development status, unaddressed feasibility issues, and desirable material properties of historic fuel systems for LEU NTP is discussed.

Composite Fuels: Graphite Structural Matrix

Composite graphite-based fuels were the first fuels developed for NTP in the United States through the Nuclear Engine for Rocket Vehicle Application (NERVA)/Rover program. Throughout the program, fuel forms evolved from dispersed UO_2 or UC_2 particle impregnated graphite plates to extruded hexagonal fuel elements containing a dispersed uranium-zirconium carbide, (U,Zr)C, fuel web with coolant channels for hydrogen flow [23]. The NERVA/Rover program was the only program to ground test fuels in NTP prototype engines, therefore composite graphite matrix fuels are the only fuel type that has been tested in a fully assembled reactor core with the prototype conditions of a nuclear thermal rocket. Compared to other materials, graphite offers the ability for exceptionally high operating temperatures, good high temperature strength, and relative ease in fuel form manufacture. Other attributes include low thermal neutron absorption (σ_a), high scattering cross section (σ_s) and a large established irradiation database/operational experience.

Graphite based fuels have acceptable thermal conductivity and high temperature strength, which allows for the reduction of temperature gradients and reliable mechanical response during operation. Due to the extensive database of operating experience, the failure modes of graphite-based fuels are well known and is reviewed elsewhere [23-26]. The largest hurdles associated with future development graphite-based fuel systems is associated with the incompatibility of graphite with the H_2 propellant, which alters the reactor power profile during operation and degrades the structural integrity of the matrix. Exposed graphite must be coated using protective

Table 1.2 Comparison of selected properties, attributes, and limiting feasibility issues of materials utilized in historic NTP development programs [45, 46].

Fuel Type	σ_s (b)	σ_a (b)	Melting Temperature (K)	Key Attributes	Limiting Feasibility Issues
Cermet				- Hot hydrogen compatibility - Low thermal absorption cross section (Mo) - High operating temperature potential (W) - High uranium fuel loading	- Vapor pressure limits to operating temperatures below 2470 K (Mo) - High DBTT - High thermal absorption cross section (W)
Molybdenum	5.71	2.48	2890		
Tungsten	4.60	18.3	3695		
Composite				- High operating temperature potential - Manufacturability - Lowest absorption cross section - Highest development status	- Chemically incompatible with hot hydrogen - Poor mechanical properties in tension
Graphite	5.55	0.0035	4000 ¹		
Carbide				- Highest operating temperature potential when in solid solution with UC - Low absorption cross section - Good hot hydrogen compatibility	- Highest DBTT - Poor thermal shock resistance - Lowest development status
ZrC	12.01	0.19	3910		
NbC	11.81	1.15	3770		
HfC	15.79	104.1	4250		
TaC	11.56	20.60	4250		

¹Sublimation temperature in vacuum

Coatings (claddings) to prevent exposure to the hot hydrogen environment and subsequent corrosion. Minimizing incurred thermal stress and dimensional instability of graphite fuels is key to maintain coating integrity. Moderate thrust (10 – 25 klbf) LEU engine designs based upon the Small Nuclear Reactor Engine (SNRE) developed during the NERVA/Rover program have been demonstrated using graphite composite fuel with a (U,Zr)C fuel web [13]. The key advantage of graphite-based fuels for LEU NTP application is the desirable neutron cross sections σ_a and σ_s of carbon, thereby allowing the structural graphite matrix to also function to moderate the neutron flux within the core in addition to use of external moderating elements.

Cermet Fuels: Refractory Metal Structural Matrix

The advantages of refractory metals molybdenum (Mo) and tungsten (W) are their capability for high temperature operation, high temperature strength, high thermal conductivity, hydrogen compatibility, and high ductility at the operating temperatures desired for NTP. Mo and W cermets with distributed uranium dioxide (UO₂) or uranium nitride (UN) fuel particles have undergone extensive development and separate effects testing through programs at Los Alamos National Laboratory (LANL), Argonne National Laboratory (ANL), NASA Lewis Research Center, and General Electric (GE) [27]. From these programs, high temperature irradiations, hot hydrogen testing, thermal cycling, and thermal shock testing has been performed. Due to the higher melting temperature and better thermal stability of W in the hydrogen environment, later fuel development focused on W-based fuels.

The development of W-matrix ceramic-metallic (cermet) fuels addressed the specific design challenges encountered in the Rover/NERVA program. W is compatible with the H₂ propellant, exhibits superior high temperature strength and extended lifetime at high temperature (endurance) [28]. The main drawbacks of W-cermet fuel are high thermal σ_a and high ductile to brittle transition temperature (DBTT), which results in difficulty in the fabrication of full-length, net-shape fuel elements. Although W has a high thermal σ_a , cermet fuels do allow for high fuel volume loadings without significantly compromising the fuel's structural integrity [29]. Most reference cermet engine designs use fuel loadings of 40 - 60 vol% within the matrix and a fast spectrum to compensate for the high natural thermal σ_a of W. LEU NTR designs using a W-cermet fueled core, developed initially under the Space Capable Cryogenic Thermal Engine (SCCTE) project, have been demonstrated [30], but require the use of external moderating elements and enrichment of natural W in the W-184 isotope. Mo is an alternative matrix candidate due to its hot H₂ compatibility and low thermal σ_a . However, due to the lower melting temperature and poorer

observed performance under thermal cycling of Mo, it has been suggested limit the system to operation temperatures of ~ 2500 K ($I_{sp} < 900$ s) [31]. W-cermet fuels have been the subject of high temperature irradiation and hot hydrogen testing through past program developments, which has led to a good understanding of fuel behavior and potential failure pathways [31-33]. The largest risks associated with the operation of W-cermet fuel systems is attributed to the vaporization and migration of UO_2 fuel during high temperature operation, which leads to loss of reactivity and structural integrity of the fuel system [33]. Modern manufacturing methods such as via SPS have demonstrated the production of tungsten cermets close to theoretical density, which is expected to assist in the retention of fuel during operation [34-36].

All Carbide: Solid Solution UC Fuels

Transition metal carbides (TMCs) have the highest known melting temperatures for all known compounds and are chemically compatible with hydrogen. Because of this, refractory carbides have been recognized to have the potential for highest NTP fuel operation temperatures (3000 – 3400K) and fuel endurance at temperature [1, 37, 38]. TMC fuel systems are typically proposed in the form a solid solution with UC to form extremely high melting temperature fuel that exhibits thermal and chemical stability in the reducing H_2 environment [25, 26, 39-42]. All-carbide solid-solution fuels (UC-ZrC, UC-NbC, UC-TaC, UC-ZrC-TaC, UC-NbC-TaC) were studied and tested extensively by the former soviet union [42, 43] and underwent US development and testing via the Nuclear Furnace (NF-1) test late in the NERVA/Rover program [40]. The most significant progress in the development of these fuel systems were undertaken by the former soviet union, designed all-carbide solid-solution fuels did not function as structural matrices and latter fuel development aimed to manufacture geometries which could better withstand the power densities and corresponding thermal loadings of the NTR core [43]. The major limitations of all-carbide fuels are their extreme brittleness and limited solubility with uranium carbide at elevated temperatures, which reduces total U-loading within the fuel [44]. No all-carbide LEU reactor design has been fully designed and proposed for NTP applications, however limited scoping studies have calculated that UC-ZrC-HfC fuels, with enriched hafnium, can form infinite lattice geometries with infinite lattice constants (k_{inf}) greater than 1.0 [22].

Refractory Carbide Material Systems for Nuclear Thermal Propulsion

Refractory carbides (RCs), including the transition metal carbides (TMCs) and SiC, are some of the highest temperature compounds with melting or sublimation temperatures in excess of 3000 K. Several RCs offer very high temperature capability along with high thermal conductivity. Development of transition metal carbide (TMC) materials systems for nuclear thermal propulsion applications dates back to the original development of NTP in the U.S. via the NERVA/Rover program (1955 – 1972). Historical NTP material reviews concluded that as long as no “free carbon” is available to interact with the hydrogen propellant, i.e. as long as TMCs are fabricated with an ideal 1:1 carbon to metal ratio (C:M) or sub stoichiometric C:M, TMCs have the potential to be highly inert under NTP operating conditions [25, 26]. Because of this, some TMC material systems have been developed previously for NTP applications including functioning as protective coatings in the NERVA/Rover program (ZrC and NbC) [2, 23, 47], insulating/structural support materials (ZrC, TaC) [2, 48, 49], as well as solid solution fuels (UC-ZrC) [40, 42]. Historic testing of RC material systems has shown their capability to withstand prototypic environments with minimal corrosive interaction with H₂. However, current availability of microstructural investigations of heritage NTP material systems is limited, manufacture feedstock and processing capabilities are outdated, or no longer available, and current design architectures require development of materials capable of withstanding higher temperatures and more demanding operating conditions in order to enable competitive performance. This results in the need to recognize and address knowledge gaps in existing materials properties data to drive informed materials selection for engine/reactor components, as well as identify and demonstrate applicable, affordable manufacture pathways while developing a detailed understanding of manufacture process impact on material performance. NTP provides a unique opportunity for the development of high performing material systems for in-core reactor components and fuel systems

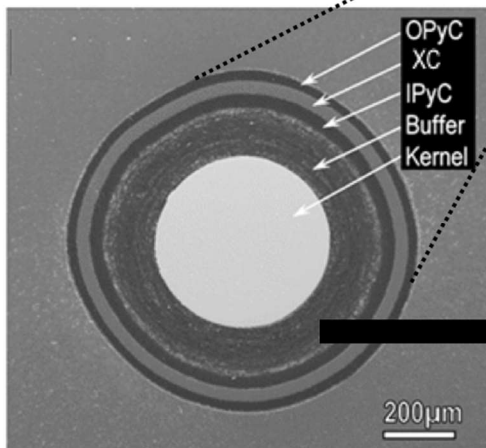
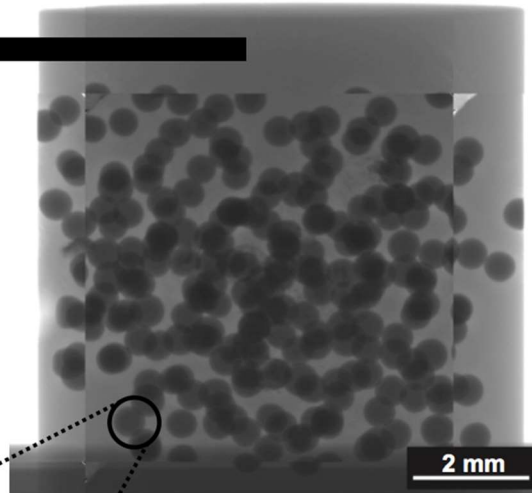
Fully Ceramic Microencapsulated Fuels for Nuclear Thermal Propulsion

Applications

Originally developed to enable very high burnups and enhanced accident tolerant fuels for terrestrial power reactors, refractory carbide fully ceramic microencapsulated (RC-FCM) fuels offer a modern, alternative fuel design for nuclear space applications [50, 51]. Composed of a structural refractory carbide matrix impregnated with coated uranium compound particles (UO₂, UC₂, UN, UC-ZrC, etc.), the RC-FCM design (figure 1.3) can be considered to be an evolutionary

Structural Refractory Carbide Matrix

- Allows for ultra high temperature operation (2350 – 3200 K)
- SiC, ZrC, TiC, and NbC matrices allow for LEU compatibility without isotopic enrichment or external moderating elements
- Offers hydrogen compatibility to protect fuel particles from hydrogen attack



Advanced TRISO

- Fuel Kernel: UO_2 or UN
- Multiple barriers of protection retain fissile fuel kernel for ultra high temperature operation (> 3000 K)
- Attenuates recoiling fission products to reduce irradiation damage of the matrix
- Refractory carbide pressure vessel layer traps fission products to prevent escape into propellant or interaction with the matrix

Figure 1.3 Fully ceramic microencapsulated (FCM) fuel systems composed of structural refractory carbide matrix and advanced TRISO particles may offer advanced tolerance to NTP operating conditions due to low cross sections and multiple barriers of protection to prevent H_2 attack of the ceramic fissile fuels (adapted from [59]).

modification of the original NERVA/Rover graphite fuel design. However, by utilizing a refractory carbide matrix: silicon carbide (SiC), titanium carbide (TiC), zirconium carbide (ZrC), niobium carbide (NbC), etc., RC-FCM fuels have the potential for enhanced tolerance to NTP operating conditions due to anticipated compatibility with the hydrogen propellant and use of coated fuel particles. Coated fuel particles, such as that of the tri-structural isotopic (TRISO) design, offer a variety of protections to the fuel to prevent degradation during operation. In addition to the inert structural matrix, multiple particle coatings act as barriers of protection against hydrogen attack of the fissile fuel kernel. Inclusion of a low-density pyrolytic carbon (PyC) buffer layer allows for attenuation of recoiling fission products to minimize fission fragment irradiation damage to the structural matrix. Discrete particle layers also help in the prevention of fissile fuel migration within the matrix and potential preferential volatilization.

An ideal NTP fuel system would be compatible with the H₂ propellant, enable operating temperatures exceeding 2500 K, minimize neutron absorption or provide neutronic moderation via a structural matrix, retain and protect fuel particles during operation, as well as minimize damage to the matrix due to fission product interaction. RC-FCM fuels have the potential to meet all of these design needs. Refractory carbides correspond to some of the highest operating temperature compounds and are anticipated to be compatible with the H₂ propellant. ZrC and NbC were originally explored for NTP applications as coatings for graphite based NERVA/Rover fuels, due to their high melting temperature (in excess of 3500 K) and anticipated hydrogen compatibility [52]. The carbon-based compounds also offer the ability to reduce parasitic neutron absorption or moderate the neutron population unlike refractory metals Mo, Ta, and W typically proposed for use in ceramic metallic (cermet) fuel systems. From previous FCM fuel development programs, particle volume loadings of greater 40% have been demonstrated in SiC matrix fuel systems [53]. High fissile fuel loading in a moderating matrix can allow viable NTP engine designs for both HEU and LEU schemes. Compared to LEU composite (graphite based) and cermet (refractory metal based) fuel systems derived from historic NTP programs, loaded refractory carbide matrix ceramic-ceramic (cercer) composite fuel systems offer increased flexibility to the designer and have the potential to enable criticality without the need for external moderating elements (tie-tubes), as demonstrated in figure 1.4.

Recent accident tolerant fuel development programs funded through the Department of Energy have investigated FCM matrix fuels for implementation in the current fleet of light water reactors and matured the development of FCM fuel systems composed of a SiC-matrix TRISO loaded pellet [50, 54-57]. Through these development activities, fuel fabrication processes have been

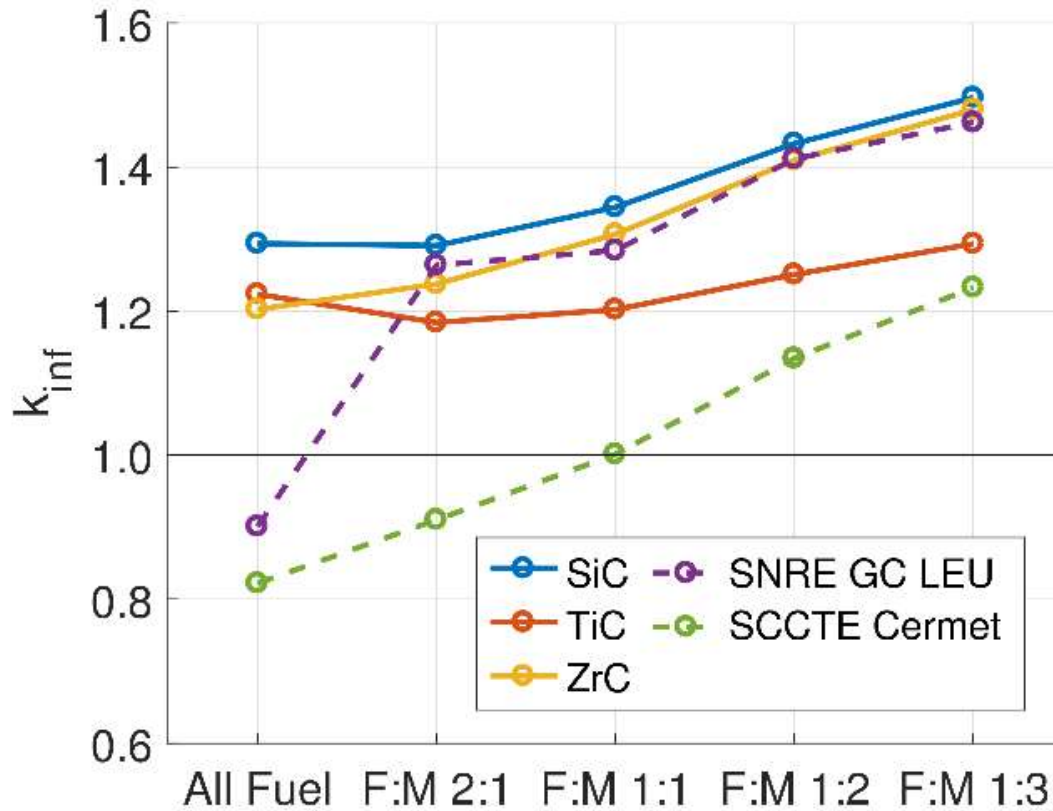


Figure 1.4 Comparison of loaded (35 vol% UO_2) refractory carbide matrix cermet fuels compared to SCCTE enriched W-184 cermet fuels (W-60 vol% UO_2) and SNRE graphite composite (GC) fuels (Graphite-35 vol% UC-ZrC) proposed for LEU NTP (data replotted from [60], further calculation details and assumptions reported in Appendix A). The infinite lattice constant k_{inf} was calculated for each fuel design with and without (all fuel) the use of $\text{ZrH}_{1.8}$ containing moderator elements. Fuel to moderator ratios (F:M) of 2:1, 1:1, 1:2, and 1:3 are probed here. In the RC-cermet cases, no external moderator is required for $k_{\text{inf}} > 1$. SNRE derived fuels perform similarly to the highest performing RC-cermet fuels once moderating elements are incorporated into the design. SCCTE type fuels require a $\text{F:M} > 1:1$ in order to achieve a $k_{\text{inf}} > 1$. A comparison of RC-cermet to RC-FCM fuel reactivity is reported in Appendix B.

matured. Current fabrication processes of SiC-FCM fuels for terrestrial power applications utilize the nano-infiltrated transient eutectic (NITE) fabrication process to reduce process temperatures and thereby reduce potential fuel particle damage. The NITE process typically requires the addition of alumina-rare earth oxide additives which reduce the necessary pellet sintering temperature (~ 1800 °C) by forming a high melting temperature eutectic composition with SiC[57]. This process results in a high-density carbide matrix with a dispersion of residual glassy eutectic compounds throughout the microstructure [58]. Therefore, a feasible development pathway exists for the fabrication of RC-FCM fuels. However, this process has been optimized for terrestrial reactor systems and no characterization of material performance in NTP relevant environments has been previously undertaken.

Research Objectives

Nuclear thermal propulsion is an in-space propulsion method capable of high specific impulse and thrust, which is desirable for crewed missions beyond LEO. Extensive development and testing have been undertaken through previous NTP development programs. From these programs, several different fuel systems including graphite composites, cermets, and solid solution carbide fuels have been demonstrated and tested to various levels of development status. Each of these fuel systems still have unresolved feasibility issues, which must be resolved in future NTP development programs. Due to desirable nuclear properties, very high melting temperatures, and anticipated hydrogen compatibility, refractory carbide matrix fuel systems are attractive alternatives to historically developed fuel systems. The fabrication of RC matrix fuels has been demonstrated recently under FCM fuel programs using the NITE sintering method. However, no experimental data exists under NTP relevant conditions, for temperatures of 2000 K and greater in a flowing hydrogen environment.

The purpose of this work is to investigate the intrinsic corrosion behavior of relevant RC materials: SiC, TiC, ZrC, and NbC in hot hydrogen to inform material selection during NTP component and fuel system design. Additionally, the impact of sintering additives utilized in the current FCM fabrication methods is assessed. This is encompassed by three major research elements described in this thesis:

- *Investigation of intrinsic stability of silicon carbide in hydrogen*

Determine the intrinsic compatibility of SiC with hydrogen at temperatures relevant to nuclear thermal propulsion using high purity, near theoretical density chemical vapor deposition (CVD) SiC. Emphasis will be placed on understanding the impact of temperature, time, and gas flow rate on the observed linear volatilization constant and identify transition regimes within the capabilities of the test rig.

- *Investigation of NITE silicon carbide performance in hot hydrogen and identification of the impact of sintering additives*

SiC-matrix fuel fabrication is currently made feasible through the NITE fabrication process. Therefore, an understanding of the volatilization behavior of NITE SiC and influence of relevant oxide additives/grain size will be attained by contrasting the behavior of NITE SiC against the intrinsic SiC response for the same test conditions.

- *Investigation of the intrinsic stability of transition metal carbides in hydrogen*

Determine the intrinsic compatibility of transition metal carbides (TiC and ZrC) with hydrogen at temperatures relevant to nuclear thermal propulsion in order to confirm models. High purity, high density (> 95%TD) carbide coupons were produced using spark plasma sintering for testing. Emphasis will be placed understanding the impact of time and exposure temperature on observed mass loss rates and sample compositional stability. Contrast the intrinsic SiC performance with transition metal carbides to evaluate candidates which have the potential for the longest lifetimes at temperature. Identify optimal regimes using these materials as alternative coating, fuel matrix, etc. candidates for NTP applications.

CHAPTER TWO - LITERATURE REVIEW

Hot Hydrogen Corrosion: Historic Corrosion Mechanisms in NTP Fuel Systems

Stability of the fuel in a relevant environment, including acceptable compatibility with the propellant, is a critical criterion for the selection of materials for use in the NTP engine. All materials will experience degradation during high temperature operation, either by corrosion, creep, recrystallization, or vaporization [61]. In order to down select materials for use in the engine, candidate materials must exhibit acceptable behavior for performance, with predictable degradation behavior that satisfies limits specified in the design window.

One of the largest technical challenges during historic fuel development programs was addressing incompatibility of the structural matrix (graphite) with the H_2 propellant [24, 62] during the NERVA/Rover program and cermet fuel development programs respectively. During the NERVA/Rover program, mid-band corrosion of the structural fuel matrix was a primary fuel degradation mechanism during operation. Due to the incompatibility of the H_2 propellant and graphite structural matrix, fuel systems developed during NERVA/Rover required protective coatings to prevent direct H_2 attack of the structural matrix. Protective coatings prevented severe attack of the matrix overall and significantly reduced corrosion in the highest temperature regions [47]. However, at the axial midline of the fuel elements (mid-band), corrosion rates were always maximized and never completely suppressed through coating and fuel development efforts of historic programs. Nearing the end of the NERVA rover program, mid-band corrosion was limited to approximately $45 \text{ mg/m}^2\text{s}$ ($\sim 16.2 \text{ mg/cm}^2\text{hr}$) with the development of a graphite composite fuel form consisting of a graphite matrix with a dispersed (U,Zr)C fuel web [40]. For future fuel development, it is desirable to identify structural matrix candidates capable of resisting interaction with hydrogen to limit corrosion rates to less than that incurred during the NERVA/Rover program.

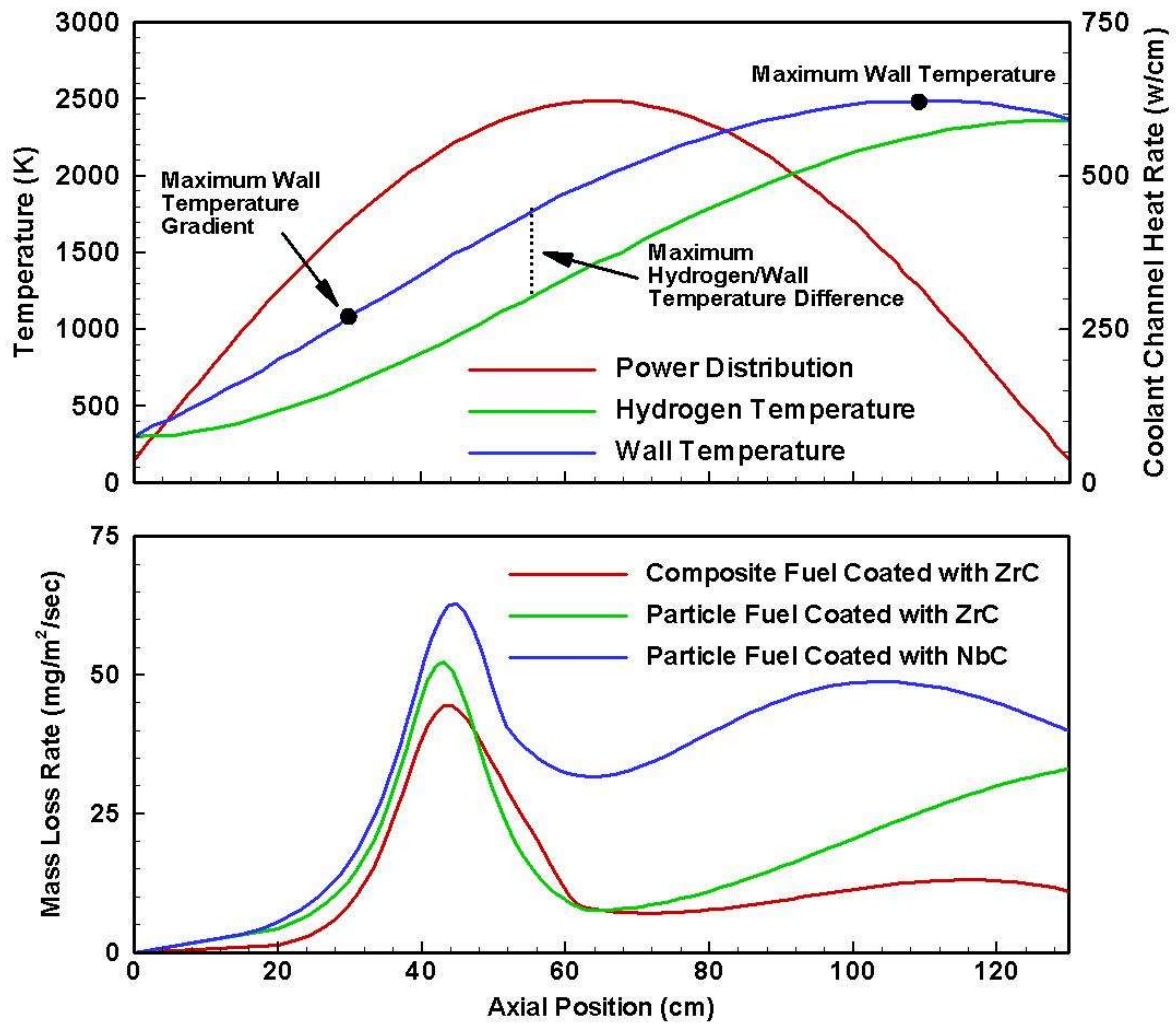


Figure 2.1 Observed mass loss behavior of NERVA/Rover graphite matrix fuels during prototypic engine tests. Future fuel development should aim to develop fuel systems capable of maximum mass loss rates less than 45 mg/m²s (~16.2 mg/cm²hr) [23, 63] (figure courtesy of NASA).

High Temperature Volatilization Behavior of Silicon Carbide

Thermodynamic calculations of SiC in pure hydrogen and moisture-containing high temperature hydrogen environments (figure 2.2) have been explored by Misra and Herbell et. al. [64, 65] for temperatures between 800 and 1625°C. These calculations have predicted three regimes in the H₂+H₂O system, depending on the moisture content. In the moisture rich regimes, both passive oxidation (II) and active attack (III) of SiC is predicted. In low moisture level or pure hydrogen environments, active attack of SiC via interaction with pure hydrogen to form hydrocarbons (primarily methane, CH₄) and free silicon (Si) or silicon hydride gasses (SiH, SiH₄) is predicted. At temperatures below 1400 °C, thermodynamic calculations predict that silicon carbide will form hydrogen carbons and solidus silicon (figure 2.3). Above 1400 °C, Si is no longer stable as a solid on the surface and is expected to contribute to the formation of SiH_x gases (1400 < T < 1600 °C) or gaseous Si (T > 1600 °C). Therefore, in the high temperature (> 1400 °C) pure hydrogen environment, SiC is predicted to be unstable and undergo active attack from H₂, which will result in mass loss during operation. Limited experimental studies have been undertaken to confirm these calculations to define SiC mass losses and limiting corrosion step information needed to define a model of SiC corrosion behavior in hydrogen at temperatures relevant to NTP. Identified corrosion studies used as a basis for defining experimental regimes of interest are outlined in the following.

Testing of SiC in pure hydrogen environments has been primarily performed using sintered alpha silicon carbide (SASC) samples (0.5 wt% sintering aids) rather than high purity SiC [66, 67]. Impurities, due to sintering additives or powder feedstock, have been known to enhance corrosion rates due to selective attack of additives [68, 69]. Therefore, the intrinsic corrosion resistance of pure SiC may be more favorable than reported loss rates. Jacobson et. al. tested SASC in 5% H₂/Ar, flow rates of 4.03, 8.07, and 16.14 cm/s, at 1300 °C for up to 24 hours in a thermogravimetric apparatus with a microbalance [67]. Total weight loss was limited to less than 1 mg/cm² and increased linearly with the square root of linear gas velocity, suggesting SiC corrosion in flowing H₂ is a mass transfer limited process. Savrun and Miller tested SASC samples at 1370°C for up to 50 hours [70]. Samples were tested under zero-stress conditions and exposed to hydrogen under static-stress conditions for 1 and 20 hours. Samples were characterized using SEM and mechanical testing to observe surface degradation to correlate to corrosion mechanisms and identify if SiC coupons were susceptible hydrogen embrittlement. Mass loss rates were low, however, sample surfaces exposed to hydrogen for up to 50 hours were observed to exhibit a microstructure indicative of grain boundary attack. It should be noted; although solid

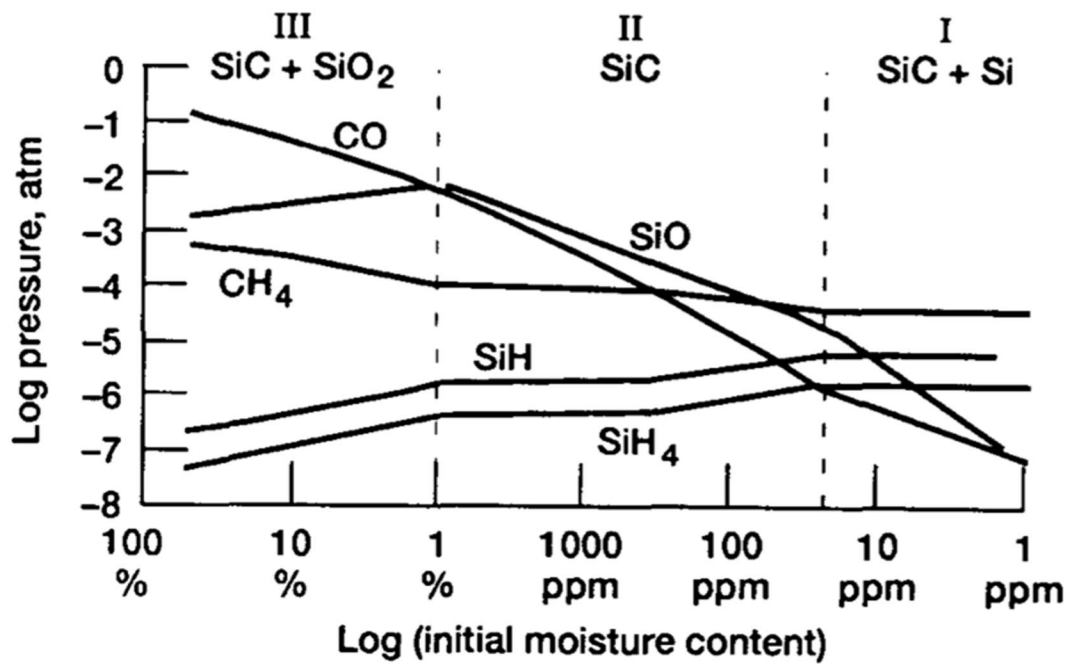


Figure 2.2 Stability of Silicon Carbide in 1 atm $H_2 + H_2O$ environments at $1400^\circ C$ (figure from [65]). At low moisture containing environments, such as relevant to pure flowing hydrogen environments, SiC is expected to undergo active attack and exhibit weight change due to volatilization/erosion corrosion.

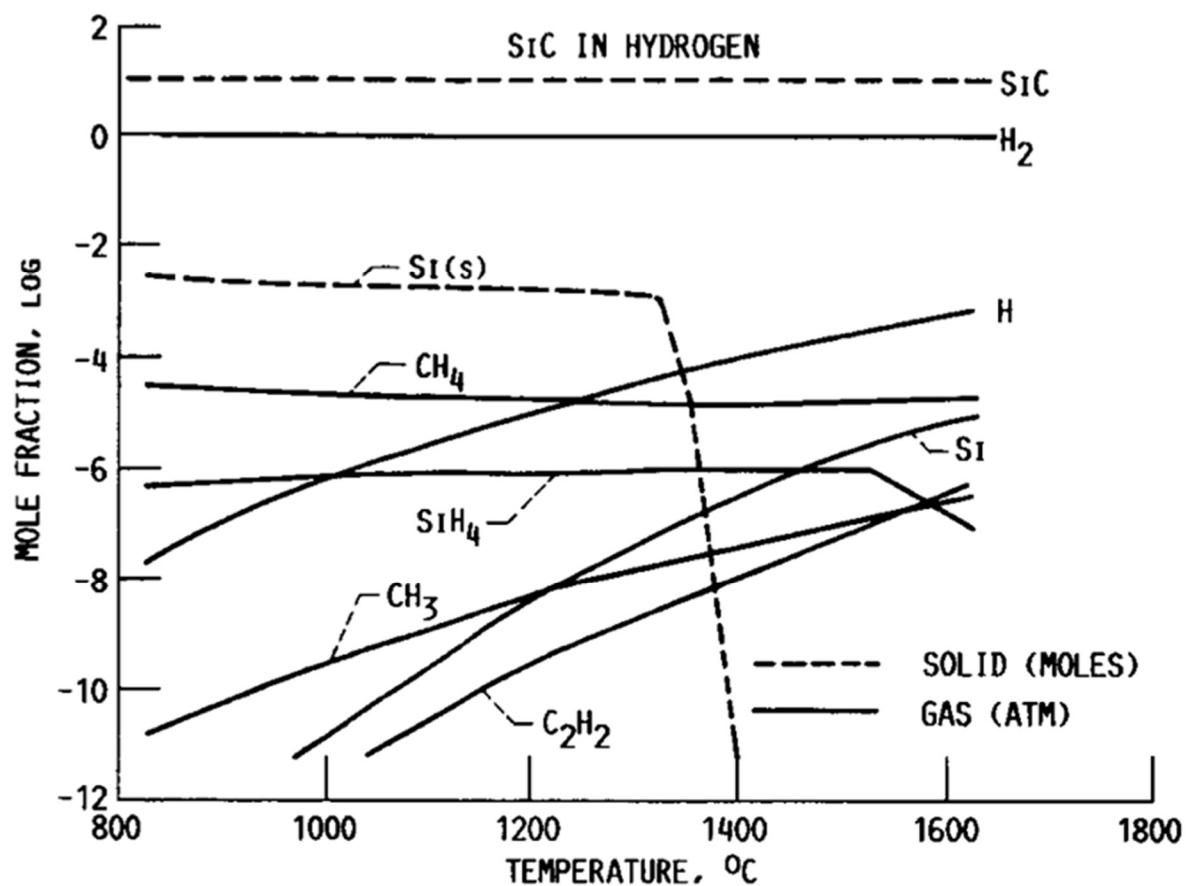


Figure 2.3 Stability of silicon carbide and relevant corrosion products in 1 atm H₂ environments at high temperatures between 800 - 1600°C (figures from [65]).

Si corrosion product formation is predicted at low temperatures (figure 2.3), no studies have reported observations of free Si ($T_m = 1414\text{ }^{\circ}\text{C}$) on the surface of SiC tested at temperatures below 1400°C .

Hallum et. al. exposed SASC and single crystal SiC samples (0.5 wt% sintering aids) to unpressurized, flowing hydrogen (25 ppm moisture content) at temperatures between $1000 - 1400\text{ }^{\circ}\text{C}$ for up to 50 hours [71], with extended testing up to 500 hours for temperatures of 1100 and $1300\text{ }^{\circ}\text{C}$. At $1100\text{ }^{\circ}\text{C}$, corrosion of the SASC was observed via grain boundary attack, which lead to grain fall out for exposures exceeding 50 hours. At the elevated test temperatures (1300 , $1400\text{ }^{\circ}\text{C}$), certain grain orientations (parallel to the basal plane) were preferentially attacked and grain fall out was observed as a result of 50-hour testing. At $1300\text{ }^{\circ}\text{C}$, SEM analysis showed a mixture of grain boundary attack and intergranular attack. As shown in in Figure 2.4, two corrosion regimes appear to be evident, as mass loss rate increasing exponentially at the highest with a transition temperature of $\sim 1300\text{ }^{\circ}\text{C}$. This is consistent with computational predictions of change in stable corrosion product however, the transition was expected closer to the melting temperature of Si ($1400\text{ }^{\circ}\text{C}$). Hallum et. al. also tested single crystal SiC samples formed via vapor deposition were tested for 50 hours at $1100\text{ }^{\circ}\text{C}$ and 20 hours at $1400\text{ }^{\circ}\text{C}$ in hydrogen with 25 ppm water content [71]. While no weight change behavior was reported, hexagonal shaped pits were observed in single crystal SiC after exposure to temperatures exceeding $1300\text{ }^{\circ}\text{C}$, confirming that at the low moisture level regime pure SiC is expected to undergo active attack.

Thermodynamic calculations predict SiC will exhibit active corrosion in flowing hydrogen and exhibit mass loss due to volatilization for temperatures relevant to NTP applications ($T > 1400\text{ }^{\circ}\text{C}$) [65]. Experimental studies have shown mass loss at temperatures of $1350\text{ }^{\circ}\text{C}$ in 5% H_2/Ar mixtures, to be very low ($<1\text{ mg/cm}^2$ over a 24 hour TGA measurement) for sintered alpha SiC (0.5 wt% impurity content) [67]. Therefore, the use of SiC in NTP applications looks promising for the short lifetimes (~ 2 hours) and pure flowing hydrogen environments. Although free Si is a predicted corrosion product, the presence of free Si has not been reported in experimental studies [64, 66, 71]. Testing at temperatures greater than $1600\text{ }^{\circ}\text{C}$ of pure SiC, is necessary to characterize expected mass losses at very high temperature regimes and predict maximum use temperatures or anticipated temperature-lifetime dependence of fuel elements.

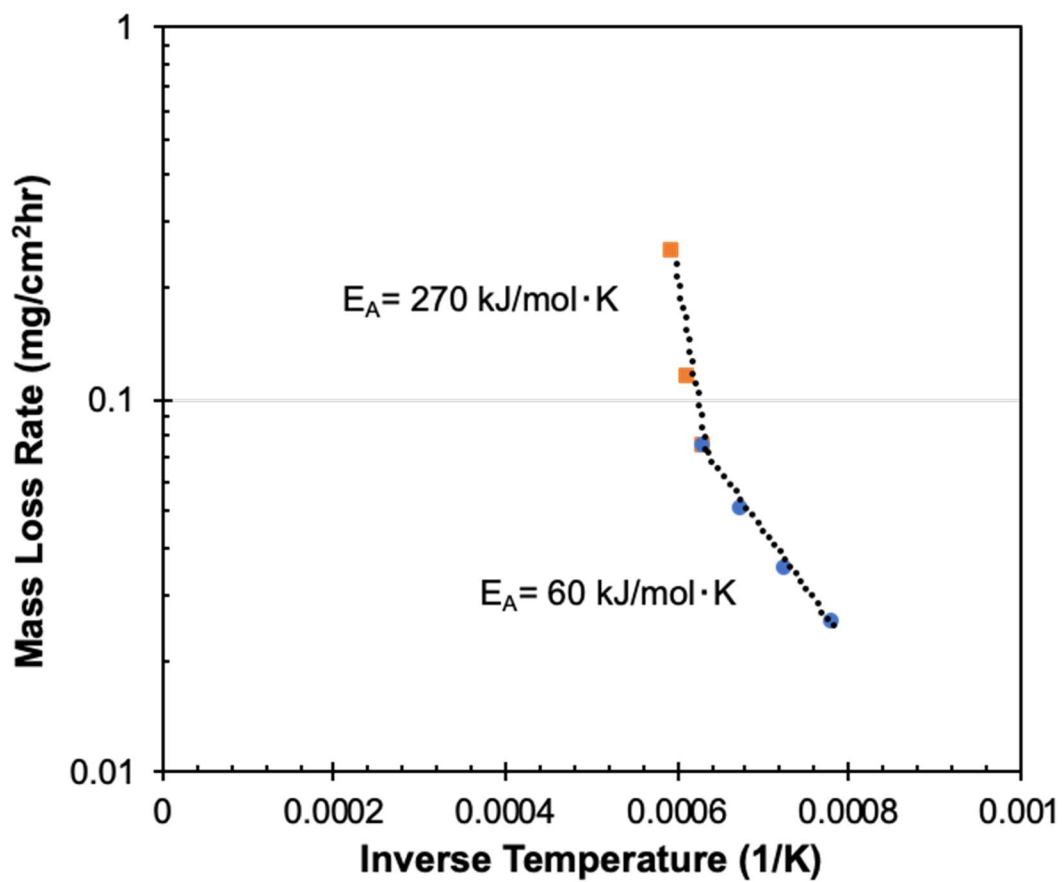


Figure 2.4 Experimentally derived mass losses of sintered alpha silicon carbide (SASC) in 1 atm H_2 environments at high temperatures between 1000 – 1400 °C show a change in activation energy at a temperature of ~1300 °C (0.0006 1/K) replotted from [72].

High Temperature Volatilization Behavior of Group IV, V Transition Metal Carbides

Vaporization behavior of the group IV, V transition metal carbides (TMCs) has been studied experimentally through high temperature vacuum vaporization experiments and Langmuir vaporization models have been augmented to predict changes in behavior due to the presence of a hydrogen atmospheres [73]. TMCs are composed of a face centered cubic NaCl structure and exhibit a wide range of stoichiometry $M_{1-x}C_{1-y}$ (figure 2.5). As a consequence, at high temperatures, as-fabricated TMCs have been characterize to vaporize incongruently until a steady state vaporization rate is achieved. In an incongruent vaporization process, there exists an initial preferential mass loss rate of carbon or metal atoms from the surface, until the local composition at the surface reaches an equilibrium with the environment, at which a steady state is achieved (figure 2.6). Once at steady state, carbon and metal atoms vaporize at a congruent rate, which maintains the surface composition. This equilibrium composition is referred to as the congruently vaporizing composition (CVC) and is dependent on the activity of the local carbon and metal atoms in the current environment as well as the diffusivity of the carbon atoms from the bulk to the surface. Using equations derived from Langmuir models, the high temperature vacuum vaporization rate of these materials can be well predicted, corresponding CVC and recession rates can be derived (figure 2.7). From these calculations, TiC is expected to exhibit much poorer corrosion resistance than ZrC for all temperatures; however, both are expected to be more stable than graphite.

The vaporization behavior of TMCs in vacuum has been modelled and validated with experimental data, which is well summarized in [73]. However, this behavior alone is not sufficient to predict material lifetimes and temperature limits. The steady state CVC is also expected to be affected by variation in pressure, flow, irradiation, and interaction of free carbon with a corrosive propellant. For example, Kempter et. al. demonstrated the effect of a 1 atmosphere helium pressure on the steady state CVC of 88% dense NbC [74]. For all temperatures, the predicted effect of the He atmosphere was to increase the carbon to metal (C:M) ratio during vaporization to a value closer to unity (figure 2.8). Diffusion rates of carbon slow as the C:M ratio increases to one. Therefore, the He environment suppresses vaporization rate in this case and longer component lifetime would be expected. In the following section, known TMC response in hydrogen environments is overviewed.

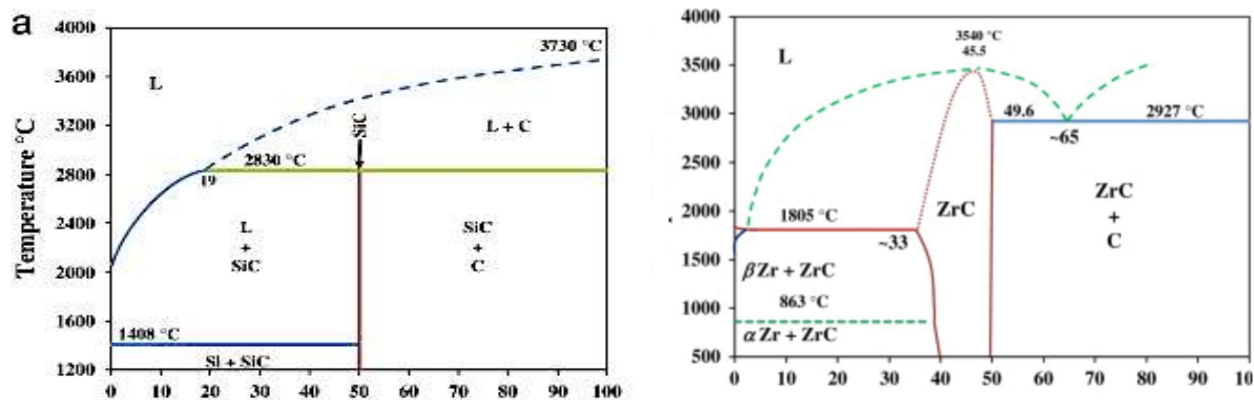


Figure 2.5 Comparison of the SiC phase diagram (left) with a typical TMC phase diagram (right). The TMC exhibits a wide range of stoichiometry which satisfies the MC phase (figures from [75]).

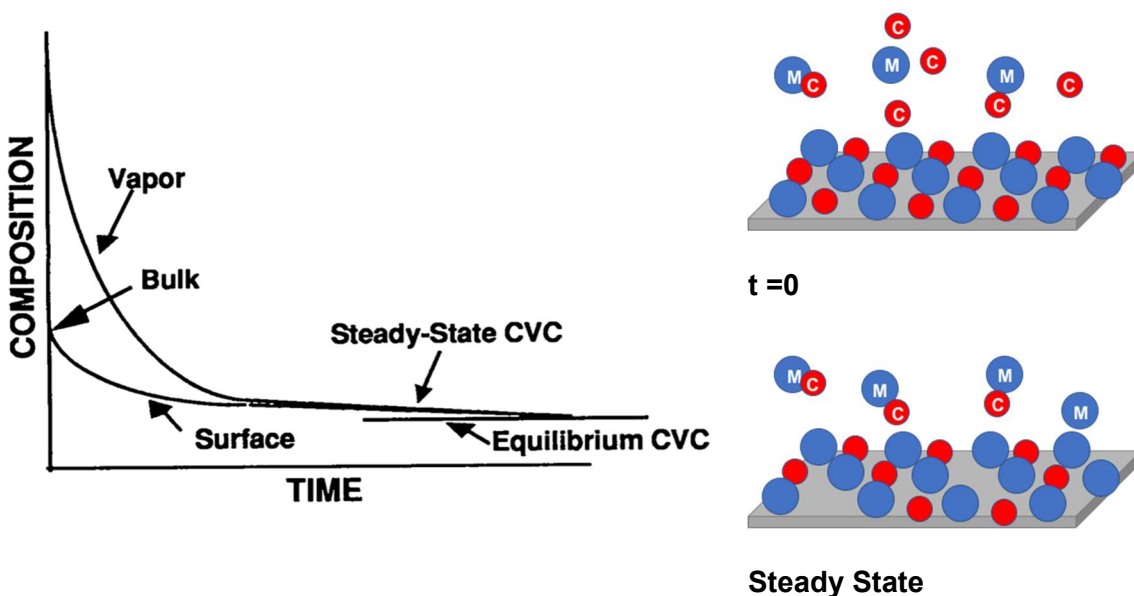


Figure 2.6 At high temperatures, TMCs (TiC, ZrC, NbC, etc.) vaporize at an incongruent rate until the surface composition reaches an equilibrium with the rate of metal and carbon atoms vaporizing from the surface. This vaporization behavior results in altered surface and bulk composition of the exposed sample based on initial sample composition and environment (left figure from [73]).

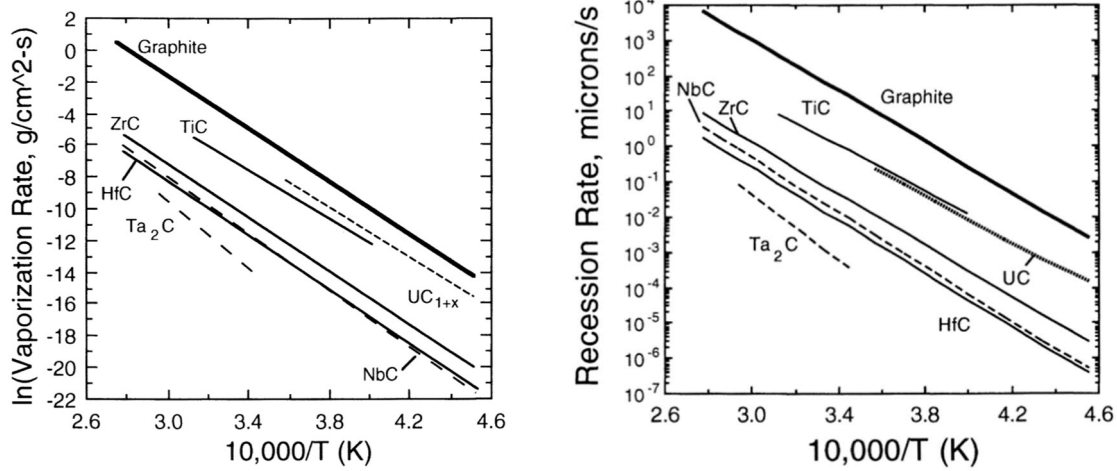


Figure 2.7 Calculated vaporization rates of relevant transition metal refractory carbide materials in vacuum at temperatures between 2175 – 3850 K. Vaporization rate is a relevant parameter to investigate for NTP fuels since it results in recession of the moderating structural matrix which alters fuel reactivity, which can result in decreased performance or evolution in power profiles (figures from [73]).

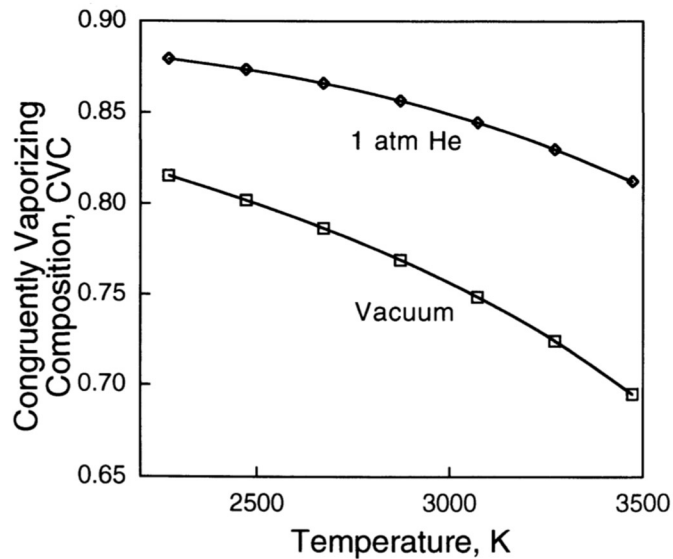


Figure 2.8 As shown above for NbC vaporization behavior in a vacuum and 1 atm He, high temperature vaporization under pressurized conditions results in different equilibrium conditions than expected in a vacuum. This results in a different equilibrium composition of the sample when exposed to different environments of varying compositions and pressures (data from [74] replotted in [73]).

High Temperature Vaporization Behavior of Fueled Transition Metal Carbides in Hydrogen

Under pressurized hydrogen flow through a cylindrical channel, such as expected at the coolant channel surface for a NTP system, CVC values are expected to be far from reaching the calculated equilibrium state derived from vaporization models. As discussed previously, several factors are expected to play a role in the compositional evolution and lifetime of refractory carbide materials in the NTP environment:

- *Interaction of the free carbon and hydrogen gas*
- *Temperature*
- *Flow Conditions (pressure, flow rate, gas purity)*
- *Bulk carbon diffusion (driven by temperature and stress gradients, irradiation)*

Non-nuclear, hot hydrogen testing at Los Alamos National Laboratory (LANL) provide the basis of current understanding of the mass loss behavior of TMCs in environments relevant to NTP [76-78]. However, these studies focused exclusively on ZrC and UC-ZrC solid solutions and were mainly focused on developing design solutions, which reduced U loss due to incongruent vaporization of the fuel. In general, the design philosophy was that (U,Zr)C behavior would exhibit the same behavior as pure ZrC as long as UC content was kept to less than 10 at% [76].

Storms tested (U,Zr)C fuels and ZrC using non-nuclear hot hydrogen flow testing and related the behavior to the state of the art vaporization models at the time [76]. Samples were hot pressed to 85% density and tested at temperatures between 2600 – 3125 K (2327 – 2852 °C), in a 1 atm hydrogen atmosphere. Similar to the role of the helium gas atmosphere, mass loss rates of bullet shaped high density (U,Zr)C in 1 atm hydrogen were found to be suppressed compared to the calculated vaporization of the material for vacuum conditions [76]. However, measured mass loss rates were approximately 40 times less than the predicted equilibrium values of best available models. Using corrected model parameters, the recalculated temperature dependent CVC at the carbide surface under the pressurized chamber conditions was shifted much closer to unity (figure 2.9). However, no microstructural evaluation was undertaken; therefore, this phenomenon could not be definitively confirmed. Mass loss rates were observed to follow an Arrhenius temperature dependence, due to the dependence of which was attributed to dependence of CVC on bulk carbon diffusivity. Unfortunately, Storms did not report test durations, and all reported mass loss rate data is assumed to characterize steady state conditions. As a result, the time dependence of CVC and impact on corresponding mass loss rates are unknown. Later reporting by MacMillan,

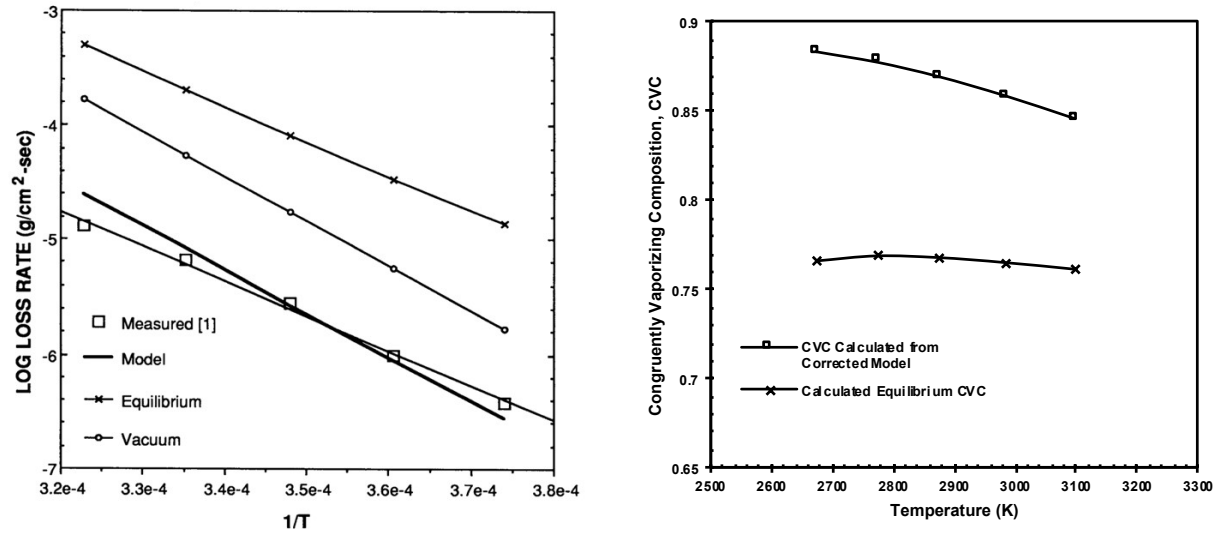


Figure 2.9 Studies of (U,Zr)C at LANL experimentally determined mass loss rates at high temperatures and related the behavior to vaporization models. Pre-existing models were not able to properly predict the CVC behavior of (U,Zr)C in hot hydrogen and led to an over prediction of mass loss rates. Experimental data collection helped to improve pre-existing models to better predict material stability and mass loss in hot hydrogen environments (replotted from data reported in [76]). summarizing LANL testing findings showed that mass loss rates of UC-ZrC was dependent on time, sometimes taking hours to reach the steady state rate (figure 2.10) [77].

It was predicted that increased pressure would increase observed mass loss rates in pure H_2 by increasing the probability of interaction with the hydrogen gas and surface carbon atoms to form hydrocarbons. However, when carbon is added to the gas, pressure would act to suppress this effect by increasing the density of hydrocarbons in the gas composition at equilibrium with the surface of the fuel. In fact, Storms' testing of (U,Zr)C tubes which contained a pressurized (10 atm) H_2 , CH_4 mixture showed that increasing pressure significantly suppressed mass loss rates for temperatures less than 3200 K (figure 2.11) [76]. Gas flow rate was expected to have a similar effect by increasing the probability that hydrocarbons would be deflected back to the surface downstream after their formation. However, Storms reported that after doubling gas flow rate, (U,Zr)C mass loss increased by 17% [76]. Storms attributed this increase to the formation of non-equilibrium conditions for the gas boundary layers at the surface. It was thought that for test conditions below 2900 – 3000 K, mass loss rates are most strongly affected by interaction of hydrogen gas and free carbon. However, this impact of increased mass flow rate could also suggest that for the selected test conditions the reported corrosion rates are limited by mass transfer.

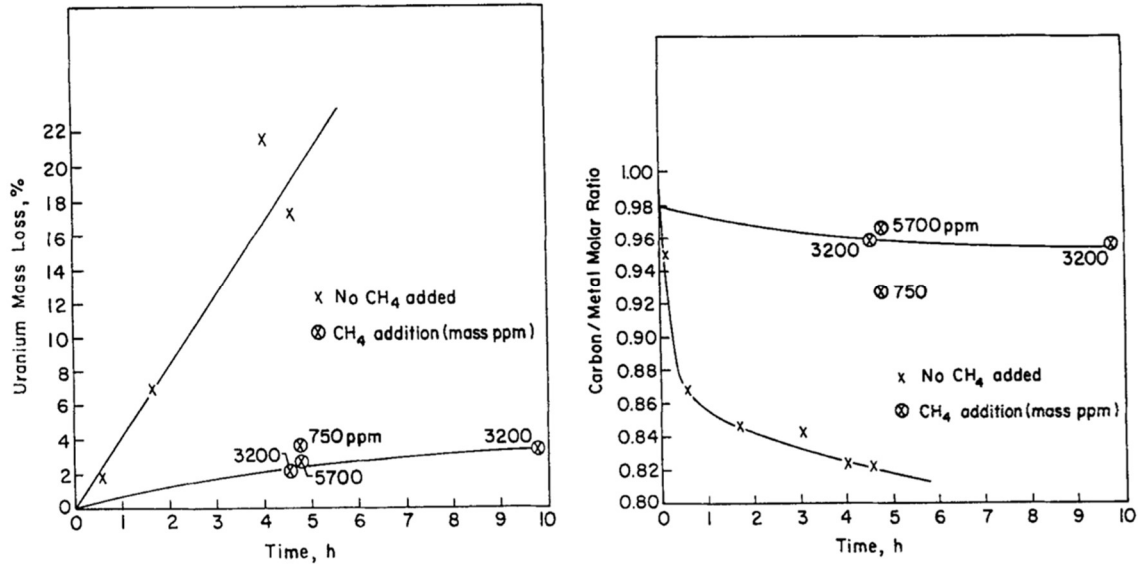


Figure 2.10 Previous studies of (U,Zr)C tested in hot hydrogen demonstrate corrosive interaction exhibits a non-linear dependence of mass loss on time and is dependent upon gas composition (figures from [77] temperature not reported).

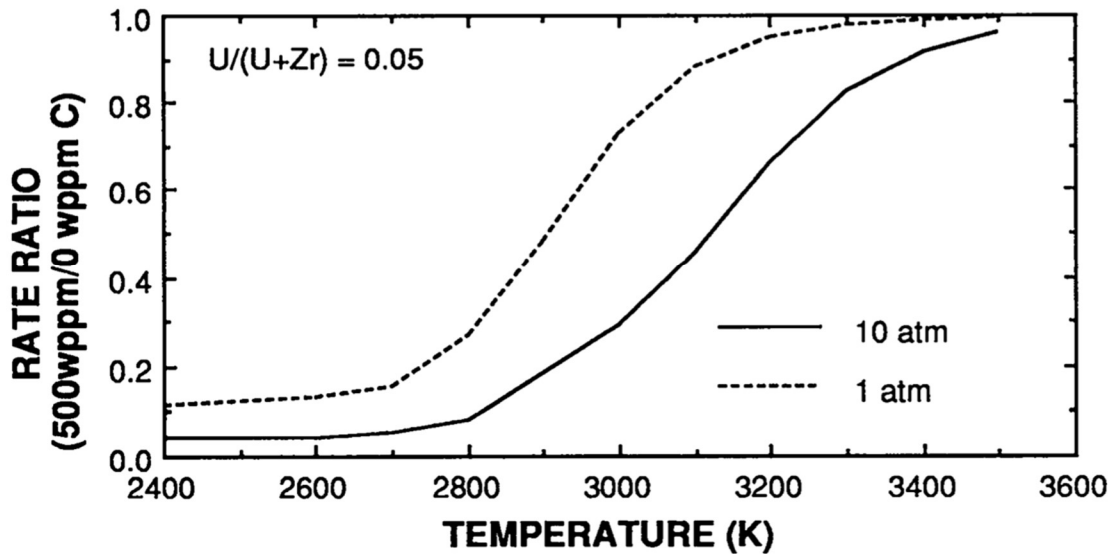


Figure 2.11 Effect of hydrogen pressure on mass loss rate observed for (U,Zr)C fuel. Mass loss is significantly reduced in the pressurized case compared to an unpressurized H₂ environment all cases at temperatures less than 3400 K (figure from [76]).

Reported Hot Hydrogen Volatilization/Vaporization Behavior of Unfueled Transition Metal Carbides

Available literature on the hydrogen compatibility behavior of transition metal refractory carbides is limited. Two studies have tested WC, NbC, HfC, ZrC, and TaC at temperatures below 1600 °C and WC, ZrC, and TaC at 2500 °C [79, 80]. Ultimately, these studies offer only qualitative information regarding the time and temperature dependence of the carbide mass loss and verification of their thermodynamic and microstructural stability in hot hydrogen at temperatures up to ~2500 °C. Mass loss data is presented as total weight change (in wt %) and no information was given about sample geometry to calculate mass loss rates. The results of these studies and microstructural characterization methodology is presented below.

Low temperature (850 - 1600 °C) hydrogen testing up to 16 hour of WC, NbC, HfC, ZrC, and TaC samples was completed by Colhron et. al. [79]. Procured samples exhibited large ranges in density/porosity (60 – 94% TD). Samples were characterized using weight loss measurements, SEM, XRD, and EDS. No information was provided on sample geometry or hydrogen flow rate. Overall, samples exhibited low mass loss, 0.015 – 4.826% total weight change (figure 2.12). Two specimens of ZrC and HfC gained weight during testing which was attributed to the pre-test vacuum baking treatment of the samples, which was intended to remove all moisture in the original sample microstructure. For low temperature testing, TaC exhibited the greatest resistance to mass loss. However, XRD spectra indicated the formation of tantalum oxide and hydride peaks following hydrogen exposure. XRD analysis showed WC exposed to hydrogen for 16 hours was converted into a mixture of pure W, WC, and unidentified peaks. NbC exhibited the greatest mass loss during low temperature hydrogen testing. This may be due to the low density (60% TD) of the obtained NbC samples, however the formation new phases were not observed by XRD.

High temperature hydrogen testing of TMCs is even more limited. ZrC, WC, and TaC were tested for two hours at ~2770 K (furnace susceptor temperature) in flowing hydrogen through programs at the Innovative Nuclear Space Power and propulsion Institute (INSPI) previously at the University of Florida [80]. Tested samples were characterized with XRD, SEM, and bulk carbon analysis using electron microprobe analysis (EMPA). Mass loss percentages were reported as total percentage mass loss, but sample geometry was not reported. WC was observed to be least stable in hydrogen and exhibited reduced density (10.91%), carbon content, as well as formation of undesirable secondary phases (W_2C) and blisters. Blistering was observed at the sample surface and attributed to the coalescence of trapped methane gas due to the carbo-reduction of

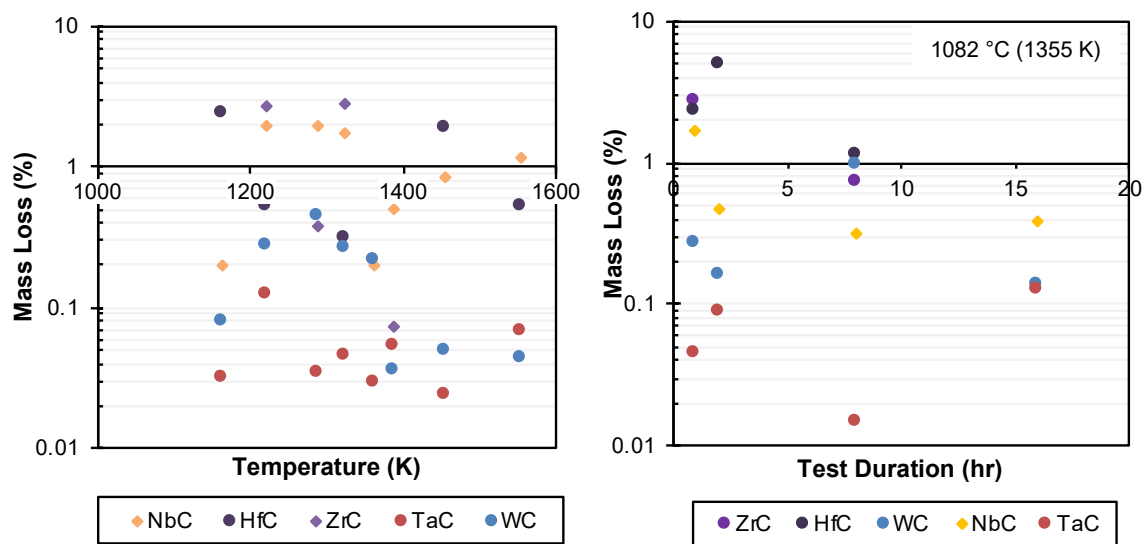


Figure 2.12 Weight change behavior of several refractory carbides after exposure to hydrogen at intermediate temperatures (850 – 1300 °C) replotted from [82].

WC by flowing hydrogen. EMPA analysis showed carbon content reduction from 12.7 wt % to 5.93 wt % and WC cross sections exhibited C depletion in the near surface region. The tested TaC sample cracked extensively as a result of testing, which was attributed to the furnace temperature transients during start up and shutdown. Carbon analysis showed reduced carbon content in TaC as a result of testing (8.14 wt % to 7.98 wt %). Total sample density reduced by 4.84% and XRD analysis showed a shift in peak positions but no formation of undesirable phases. ZrC showed most microstructural stability and least mass loss at temperatures. As produced ZrC samples were manufactured hypostoichiometric in carbon, however no statistically significant differences in carbon content or density were observed as a result of testing.

Behavior of TMCs under hot hydrogen has been most extensively investigated via testing of (U,Zr)C fuels in historic LANL NERVA/ROVER programs [76, 77]. In these studies, it was found (U,Zr)C fuels experience active attack in a flowing hydrogen environment and appear to be mass transfer limited, due to mass loss dependence on gas flow rate. However, UC was often preferentially lost from the fuel, accelerating apparent corrosion rate, and no microstructural evaluation was reported. These mechanisms should be explored and confirmed for non-uranium containing TMCs. Due to the wide range in stoichiometry allowed by the transition metal carbides, an evolution in the composition of the matrix material is expected [73, 81]. Mass losses are expected to exhibit an Arrhenius temperature dependence due to dependence on the diffusion of carbon within the matrix to satisfy the CVC during vaporization. Evolution of surface and bulk compositions with time for a given temperature are predicted to vary pretty dramatically, even for short time frames (~hours) [73, 77]. For scoping using non-nuclear hot hydrogen testing, these compositions are dependent on temperature, gas composition, pressure, and flow conditions. Transition metal carbides have been tested in hydrogen for some temperature ranges of interest to the engine. Ultimately, these studies offer only qualitative information of the time and temperature dependence of the carbide mass loss and verification of their thermodynamic and microstructural stability in hot hydrogen at 2500 °C. Models predict low TMC vaporization and long lifetimes at the temperatures of interest to NTP [76]. However, although promising, the kinetic behavior of these materials for the temperatures and time frames of interest to the engine remains uncharacterized (figure 2.13).

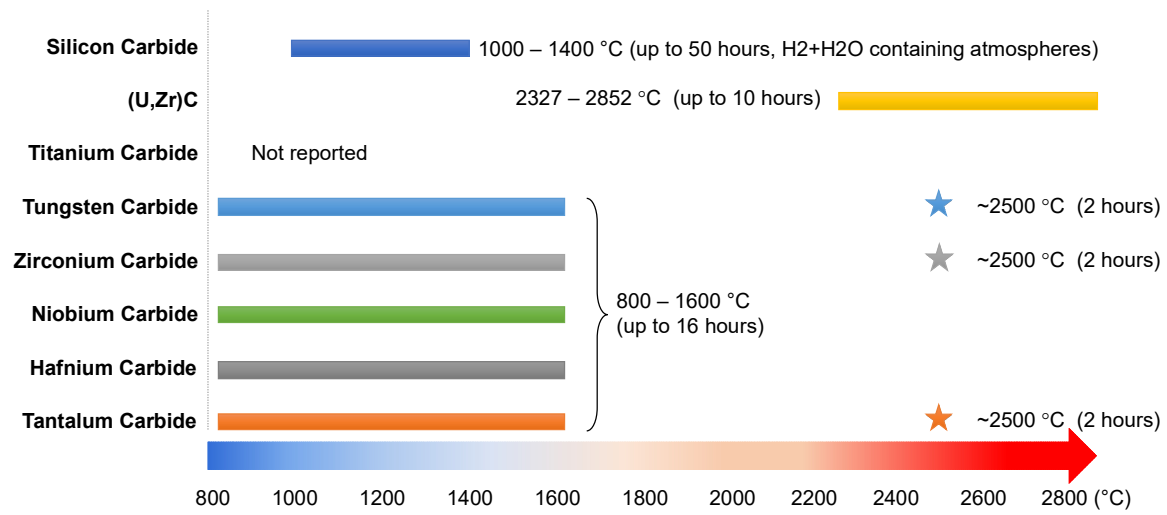


Figure 2.13 Summary of available literature data on the corrosion behavior of refractory carbide materials in hot hydrogen for temperatures relevant to nuclear thermal propulsion.

CHAPTER THREE - THERMODYNAMIC ANALYSIS

Free Energy Minimization Calculations

The observed and calculated mass behavior of silicon carbide (SiC) and transition metal carbides (TMCs) has been discussed in chapter 2. Computational simulations [66, 83] and experimental scoping studies [68, 72, 84] have shown SiC is unstable in flowing hydrogen and will decompose to form free Si and free C. Experimental studies of the transition metal carbides in flowing hydrogen have shown degradation of the TMC microstructure in flowing hydrogen and proposed a model of TMC degradation in hot hydrogen to be limited by vaporization of free metal and carbon from the sample surface. Computational studies of the thermodynamic stability of the SiC-H₂ system have been performed by Misra to temperatures up to 1600 °C [83]. These studies have calculated silicon hydrides are less stable than free Si at temperatures exceeding 1400 °C (1773 K) and decomposed Si leaves the surface as Si vapor, while free C may readily react with the gas stream to form hydrocarbons (primarily CH₄). However, thermodynamic calculations of SiC and the transition metal carbides have not been performed for the complete range of temperatures relevant to NTP applications. Therefore, in order to identify the primary corrosion products and predict potential compatibility with the hydrogen environment, it was desired to calculate the thermodynamic stability of SiC, TiC, and ZrC.

All calculations were performed using Equilib-Web, a Gibbs free energy minimization program, which calculates the most stable products for any set of reactants. Equilib-Web uses FactSage™ databases for pure substances [85]. These calculations only consider pure solids and ideal gas phases, charged species and non-ideal solutions are not considered. In table 3.1, a list of products considered for each reactant calculation is presented. For each calculation, 1 mole of solid reactant and 10 moles of hydrogen were reacted at 1 atmosphere (atm) pressure for temperatures between 1750 – 2750 K. Figures 3.1. – 3.3 show the calculated product species from SiC, TiC, and ZrC reactions with hydrogen.

Calculations for SiC expand upon the previous data set calculated by Misra et. al. and Eckel et. al. SiC is predicted to decompose in the high temperature hydrogen environment with favorable reaction products of free Si vapor and hydrocarbons. For temperatures less than 2100 K, CH₄ is the favorable hydrocarbon formed from SiC decomposition:

Table 3.1. Listing of gas species and pure solids considered in thermodynamic calculations

	SiC + H₂	TiC + H₂	ZrC+ H₂
Gases Species	H ₂ , H Si _(g) , Si ₂ , Si ₃ SiH, SiH ₄ SiC, Si ₂ C, SiC ₂ C ₂ H ₂ , C ₂ H, CH ₃ , CH ₄ , CH ₂ , C ₂ H ₃ , C ₂ H ₄ , CH, C ₂ H ₅ C, C ₂ , C ₃ , C ₄ , C ₅	H ₂ , H Ti _(g) C ₂ H ₂ , C ₂ H, CH ₃ , CH ₄ , CH ₂ , C ₂ H ₃ , C ₂ H ₄ , CH, C ₂ H ₅ C, C ₂ , C ₃ , C ₄ , C ₅	H ₂ , H Zr _(g) ZrH C ₂ H ₂ , C ₂ H, CH ₃ , CH ₄ , CH ₂ , C ₂ H ₃ , C ₂ H ₄ , CH, C ₂ H ₅ C, C ₂ , C ₃ , C ₄ , C ₅
Pure Solids	β-SiC, α-SiC Graphite Diamond Si _(l) , Si _(s)	TiC Graphite Diamond Ti(l), α-Ti, β-Ti TiH ₂	ZrC, ZrC _(l) Graphite Diamond Zr(l), α-Zr, β-Zr ZrH ₂

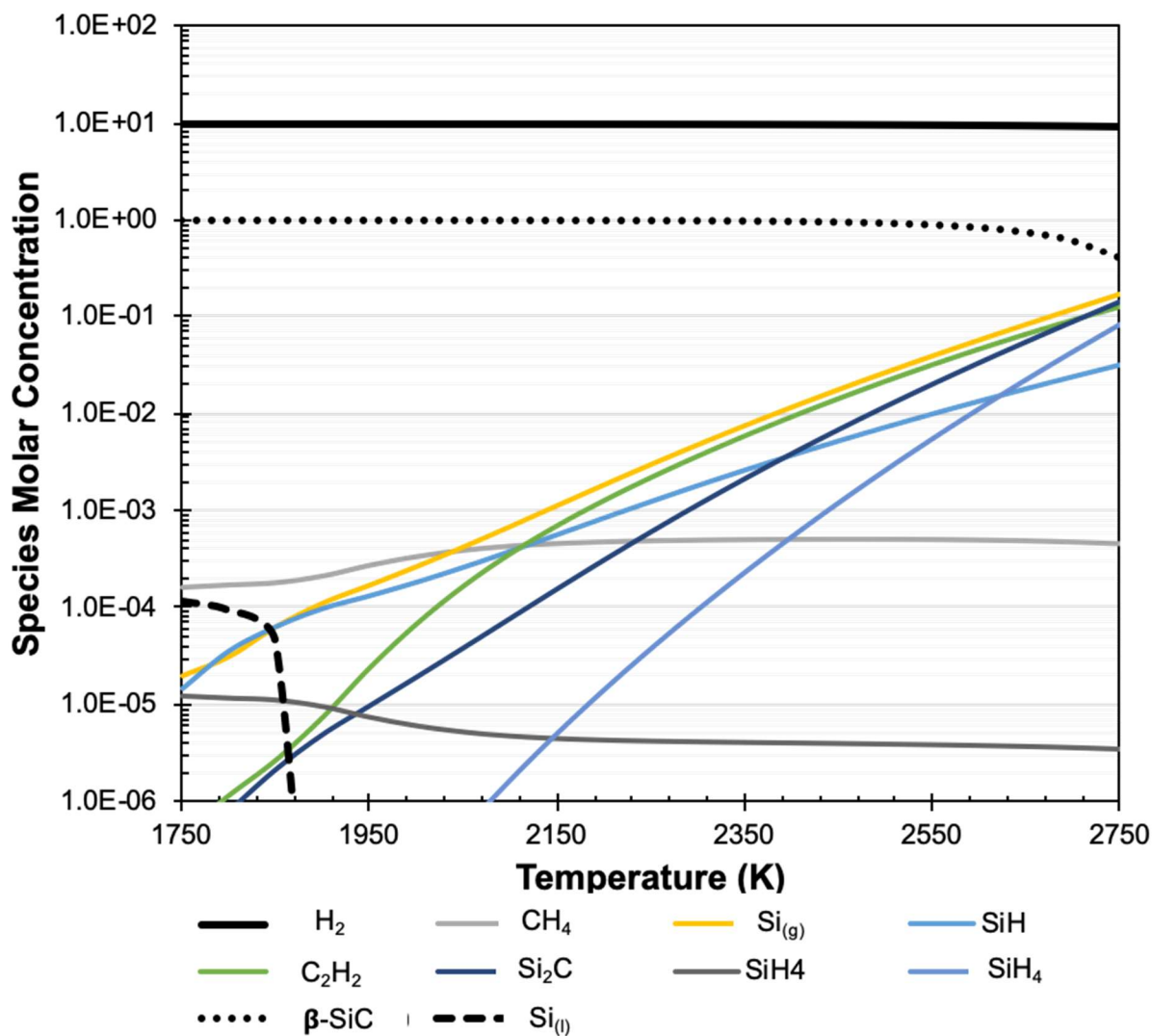


Figure 3.1 Predicted thermodynamic stability of SiC in hydrogen. Gibbs free energy minimization calculations were performed using 1 mole SiC and 10 mole H_2 reactants at a pressure of 1 atm for temperatures of 1750 – 2750 K.

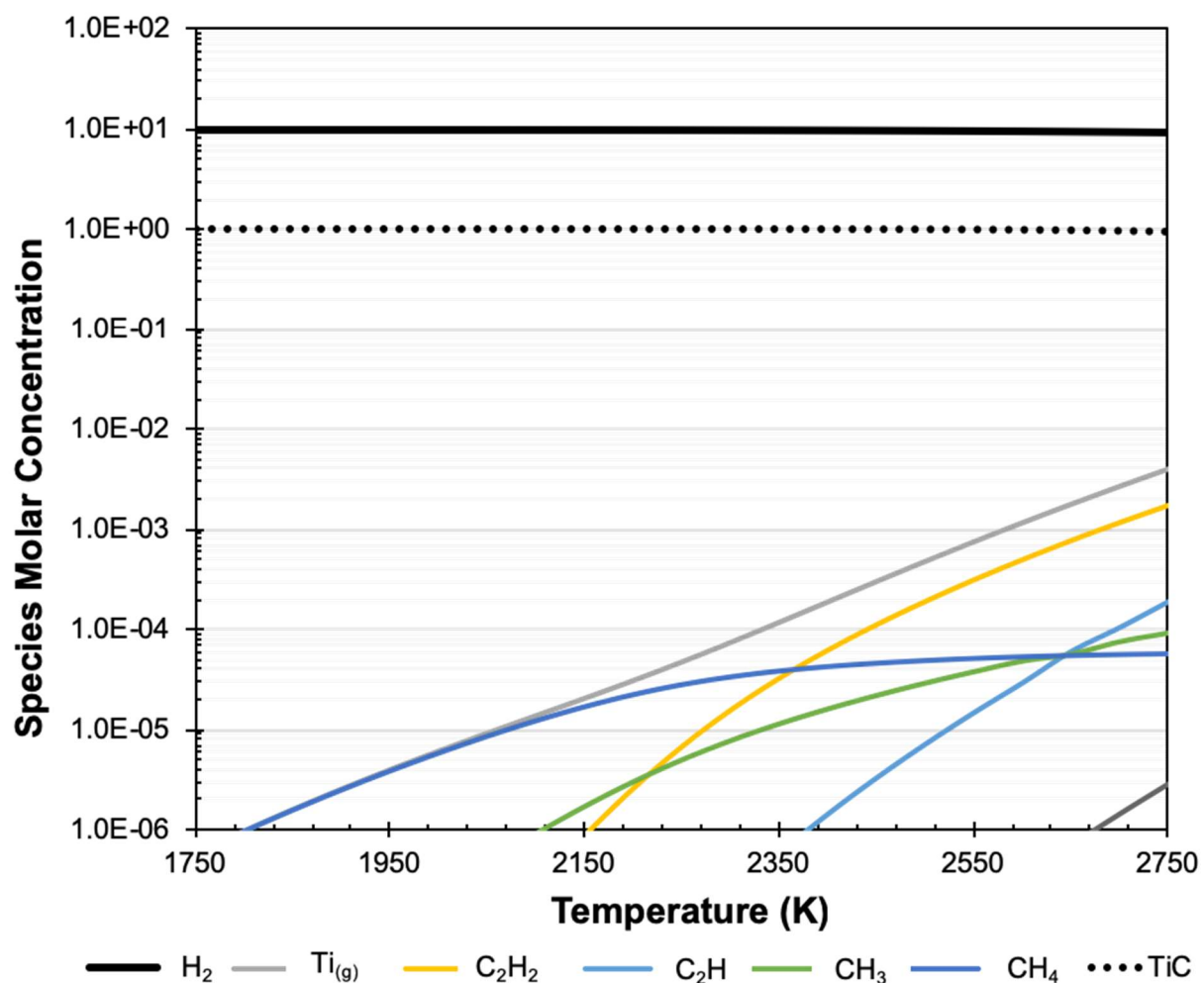


Figure 3.2 Predicted thermodynamic stability of TiC in hydrogen. Gibbs free energy minimization calculations were performed using 1 mole TiC and 10 mole H_2 reactants at a pressure of 1 atm for temperatures of 1750 – 2750 K.

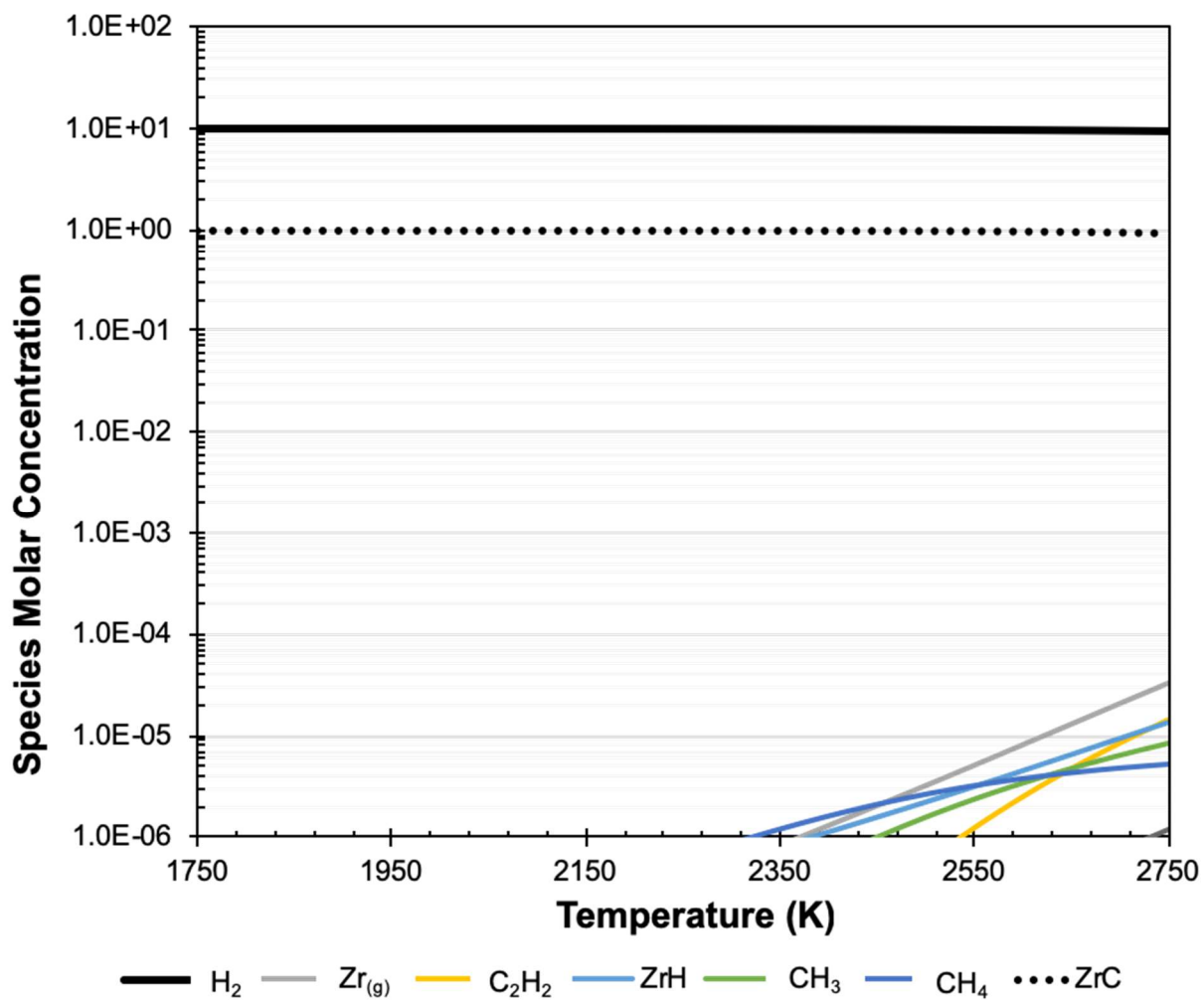


Figure 3.3 Predicted thermodynamic stability of ZrC in hydrogen. Gibbs free energy minimization calculations were performed using 1 mole ZrC and 10 mole H_2 reactants at a pressure of 1 atm for temperatures of 1750 – 2750 K.



At temperatures above 2100 K, reaction of free carbon with hydrogen to form C_2H_2 becomes more favorable:



Calculations performed for TiC show in general, TiC exhibits greater thermodynamic stability than SiC. All calculated product gas species are approximately an order of magnitude less than SiC product gas species. Similar to the SiC system, TiC is also expected to decompose in the high temperature hydrogen environment to form free Ti vapor and hydrocarbons. At temperatures less than 2350 K, CH_4 is the most stable hydrocarbon formed from the TiC hydrogen reaction:



At temperatures above 2350 K, reaction of free carbon with hydrogen to form C_2H_2 becomes more favorable:



ZrC was predicted to be the most stable in the hydrogen environment, the partial pressures of the product gas species were calculated to be less than 10^{-5} atm over the entire temperature range, indicating good stability in hydrogen. At very high temperatures, exceeding :



Where the most probable hydrocarbons (C_xH_y) are: CH_4 , C_2H_2 , and CH_3 .

Boundary Layer Limited Mass Transport Calculations

The stability of SiC, TiC, and ZrC in a hydrogen environment has been evaluated. In general,

The basics steps to decomposition of the refractory carbides in very high temperature ($T > 2000$ K) hydrogen are as follows:

1. *Sample decomposition into free carbon and free metal at the surface*
2. *Interaction of free carbon with the hydrogen gas steam to form volatile hydrocarbons (CH_4 , C_2H_2 , and CH_3)*
3. *Vaporization of free metal from the surface or interaction of the free metal with the hydrogen gas stream to form hydrides.*

This can be characterized as a volatilization reaction, a reaction of a solid sample to form a gaseous or unstable reaction product, which results in subsequent dissolution of products into the gas stream. At extremely high temperatures, all surfaces vaporize at a rate governed by the activity at the sample surface compared to its environment, resulting in loss of surface atoms and dissolution of the sample surface into the environment. Both of these processes result in active corrosion of the surface, resulting in a steady state mass loss from the surface.

Experimental observations from Jacobson et. al. and Storms et. al. have shown that the mass loss behavior exhibits a direct dependence on gas flow rate which indicates corrosion kinetics are governed by external mass transport [67, 76]. In an external mass transport limited process, sample corrosion is governed by gas transport of gaseous species from the sample surface across the boundary layer to the bulk of the gas stream. The flux of the gaseous species i from the surface can be expressed as (Eq. 3.6) [86]:

$$J_i = \frac{D_i \Delta p_i}{\delta RT} = -\frac{h_i \Delta p_i}{RT} \quad (\text{Eq. 3.6})$$

J_i – mass flux D_i – diffusion coefficient δ – boundary layer thickness

Δp_i – difference in partial pressure of gas species i at the surface and the bulk gas stream

R – gas constant T – temperature h_i – mass transfer coefficient

This shows that transport through the boundary layer is dependent on mass diffusivity, partial pressure of the limiting gas species and boundary layer thickness. The boundary layer is dependent upon the properties of the reactant gas stream (Eq. 3.7) [86]:

$$\delta = \frac{L}{Sh} \quad (\text{Eq. 3.7})$$

δ – boundary layer thickness Sh – Sherwood number L – characteristic length

The Sherwood number (Eq. 3.8) is a dimensionless number representing the ratio of convective mass transfer to diffusive mass transport and is a function of both the Reynold's number (Re) and Schmidt number (Sc) [87]:

$$Sh = \frac{h}{D/L} = f(Re, Sc) \quad (\text{Eq. 3.8})$$

h – mass transfer coefficient D – diffusion coefficient L – characteristic length
 Re – Reynold's number Sc – Schmidt number

The Reynold's number (Re) represents the ratio of inertial force to viscous force of the gas stream (Eq. 3.9) [87]:

$$Re = \frac{\rho v L}{\mu} \quad (\text{Eq. 3.9})$$

ρ – gas stream density v – gas velocity L – characteristic length μ – dynamic viscosity

The Schmidt number (Sc) represents the ratio of momentum diffusivity and mass diffusivity (Eq. 3.10) [87]:

$$Sc = \frac{\mu}{\rho D} \quad (\text{Eq. 3.10})$$

μ – dynamic viscosity ρ – gas stream density D – diffusion coefficient

For the given experimental setup and sample geometry, the Sherwood number was evaluated using the following correlation previously used by Butt et. al. for a bullet geometry in axial flow (Eq. 3.11) [88]:

$$Sh = 0.700 Re^{1/2} Sc^{1/3} \quad (\text{Eq. 3.11})$$

Where the characteristic length, L , is evaluated as the sample diameter.

Equation 3.8 may be rearranged to solve for convective mass transfer coefficient (h) as shown in Equation 3.12 [87]:

$$h = \frac{D_i}{L} Sh = k_x (C_s - C_\infty) \quad (\text{Eq. 3.12})$$

k_x – rate constant C_s – gas species concentration at the surface C_∞ – gas species concentration in the gas stream far from the surface

The mass transport coefficient allows for a correlation of the experimentally derived rate constant to analytically determined mass fluxes from the sample surface and is directly proportional to the diffusion coefficient (D) and the Sherwood number (Sh) and inversely proportional to a characteristic length of the sample (L). While the Sherwood number describes the dependence of mass transport on the gas stream, removal of the product gas species from the surface is also dependent upon the diffusion coefficient. The diffusion coefficient for the diffusion of gas i through a medium j may be calculated for ideal gases using Chapman-Enskog theory (Eq. 3.13) [87]:

$$D_{ij} = \frac{0.0018583}{p} \sqrt{T^3 \frac{(M_i + M_j)}{M_j M_i}} \frac{1}{\sigma_{ij}^2 \Omega_D} \quad (\text{Eq. 3.13})$$

D_{ij} – diffusion coefficient p – pressure T – temperature

M – molecular mass σ_{ij} – intermolecular separation distance Ω_D – Lennard Jones potential

The Lennard Jones potential was approximated as (Eq. 3.14) [69]:

$$\Omega_D = 1.2 \left(\frac{kT}{\varepsilon_{ij}} \right)^{-0.17} \quad (\text{Eq. 3.14})$$

k – boltzman constant T – temperature ε_{ij} – depth of potential well

The Lennard Jones parameters can be approximated as (Eq. 3.15) [87]:

$$\sigma_{ij} \approx \frac{1}{2} (\sigma_{ii} + \sigma_{jj}) \quad (\text{Eq. 3.15})$$

and

$$\frac{\varepsilon_{ij}}{k} \approx \sqrt{\frac{\varepsilon_{ii}}{k} \times \frac{\varepsilon_{jj}}{k}} \quad (\text{Eq. 3.16})$$

Both Lennard Jones parameters σ and $\frac{\varepsilon}{k}$ are tabulated for the gaseous species of interest [87, 89-91].

The calculated boundary layer-controlled fluxes and resulting SiC mass loss rates for primary corrosion products of SiC, TiC, and ZrC are shown in figures 3.4 – 3.6, assuming a 0.25 inch diameter sample geometry. Upper use temperature for ceramics in pure and wet hydrogen environments for turbine applications has been evaluated by limiting gas species partial pressure to 10^{-6} atm[65]. Since for NTP applications, component lifetime is much shorter than typical engineering applications, increasing the limiting partial pressure may be acceptable. By correlating predicted mass losses with historically derived limits, upper use temperatures of SiC, TiC, and ZrC can be derived. Predicted mass loss rates of SiC exceed historic limits at temperatures of approximately 2400 K for either $\text{Si}_{(g)}$ or C_2H_2 controlled corrosion. For TiC, predicted rates exceed historic values at temperature of approximately 2700 K for C_2H_2 controlled corrosion or temperatures exceeding 2750 K if $\text{Ti}_{(g)}$ is rate controlling. ZrC is predicted to be acceptable for use beyond 2750 K for all predicted gaseous species. Experimental data should aim to verify controlling corrosion mechanisms to allow for informed models to predict material stability and lifetime.

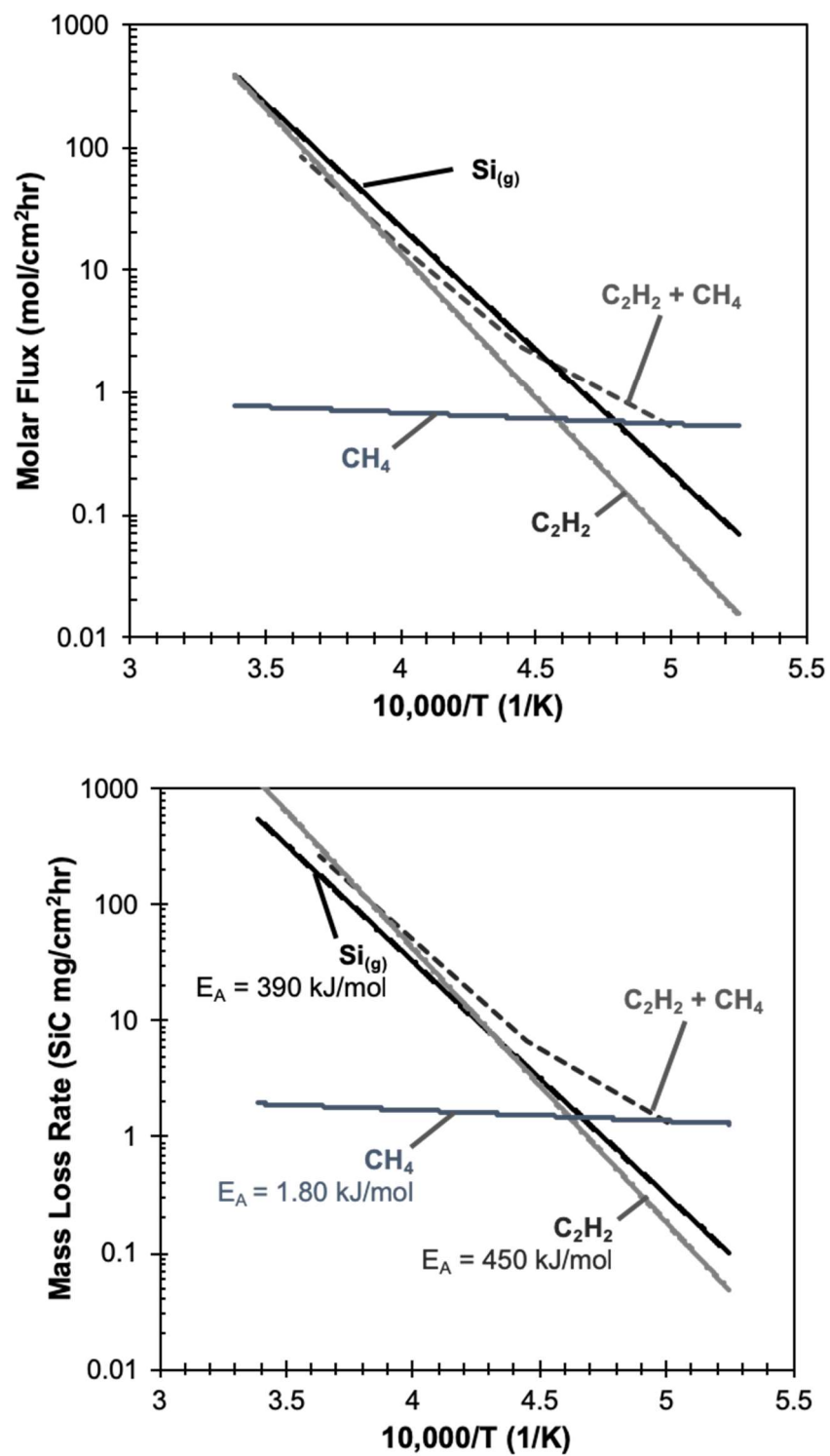


Figure 3.4 Predicted mass fluxes (top) and loss rates of SiC (bottom) in hydrogen with various limiting gas species (Si, CH₄, C₂H₂).

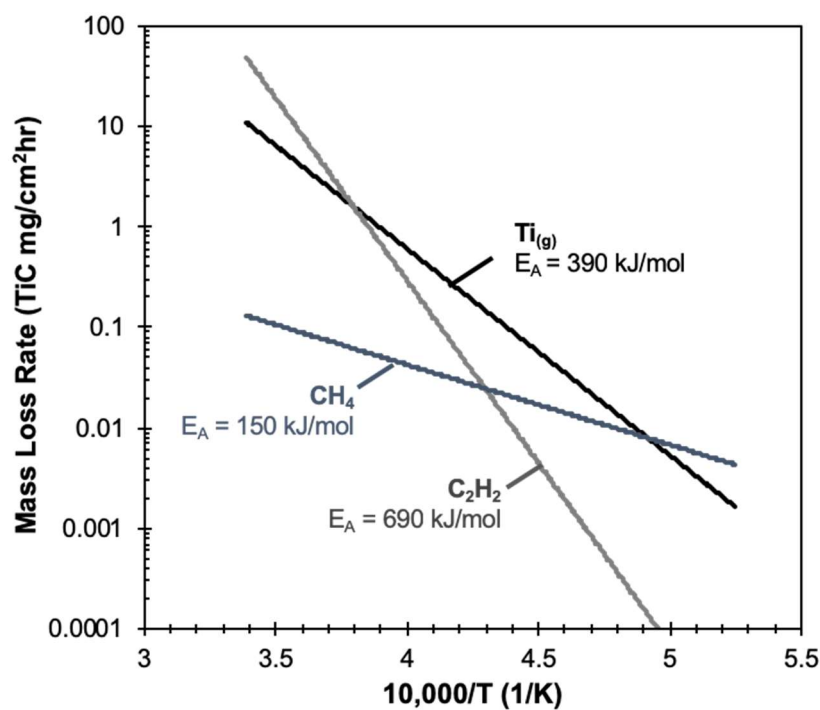
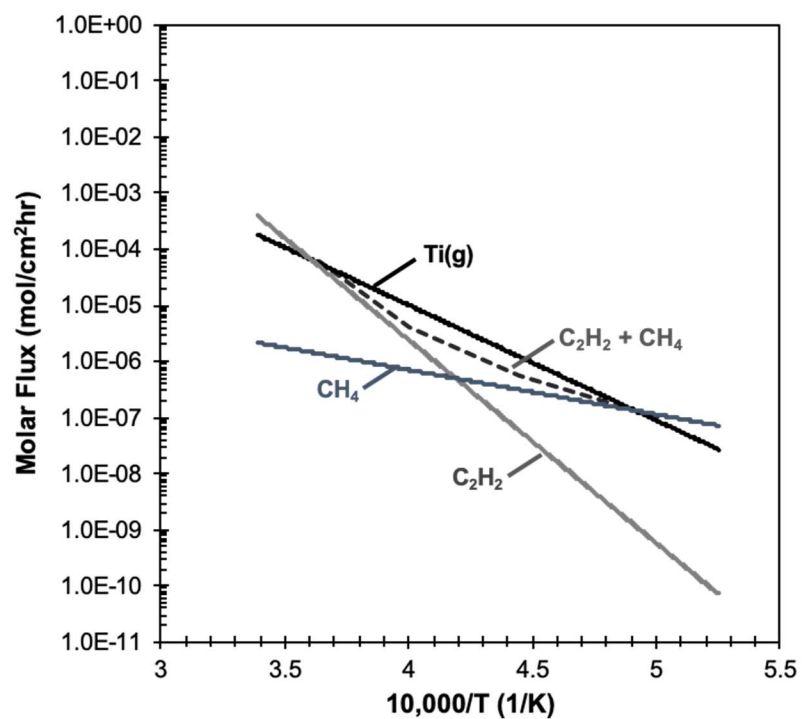


Figure 3.5 Predicted mass fluxes (top) and loss rates of TiC (bottom) in hydrogen with various limiting gas species (Ti, CH_4 , C_2H_2).

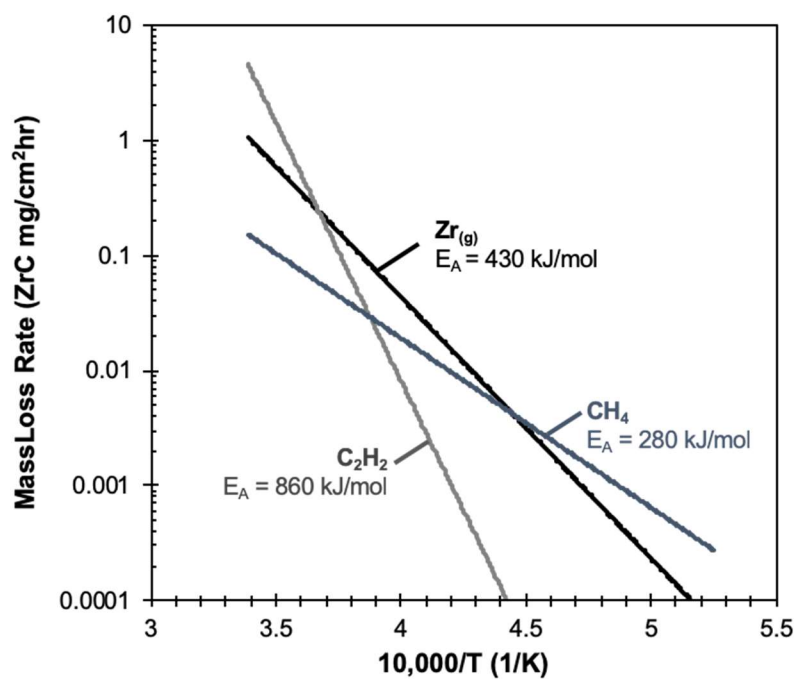
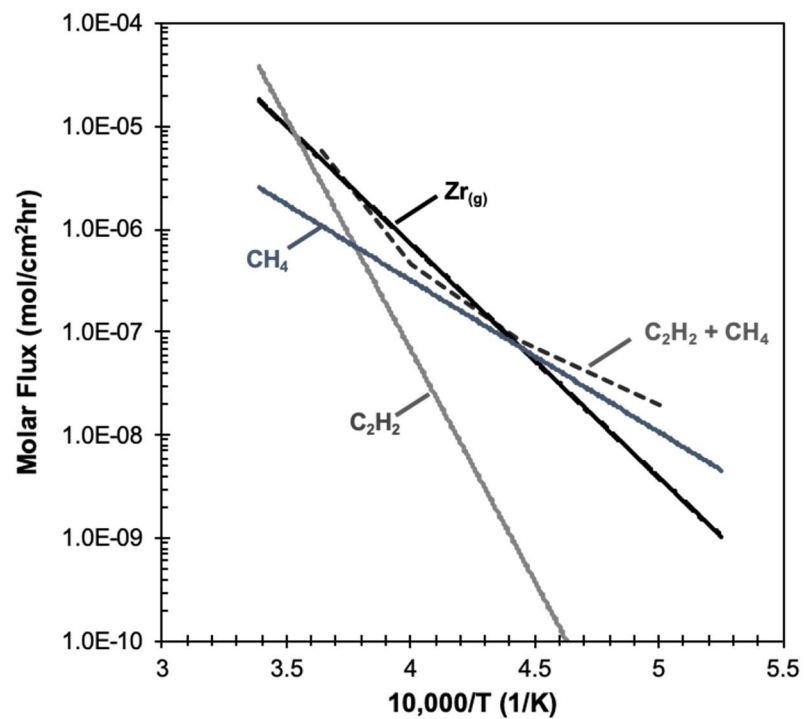


Figure 3.6 Predicted mass losses of ZrC in hydrogen with limiting gas species (Zr , CH_4 , CH_3 , C_2H_2).

CHAPTER FOUR - EXPERIMENTAL DESCRIPTION

Experimental Set Up

Hot hydrogen testing was performed at NASA Marshall Spaceflight Center using the Compact Fuel Element Environmental Test (CFEET) facility, shown in figure 4.1. CFEET is a custom designed flowing hydrogen induction furnace utilized for verification testing of candidate NTP fuel forms for NASA nuclear thermal propulsion programs [92]. CFEET was designed to test subscale, maximum length of 4.00 inches and diameter of 1.00 inches, nuclear fuels in order to rapidly screen and optimize manufacture process parameters and candidate materials for NTP applications. Current CFEET capabilities are listed in figure 4.2. The specialized facilities at NASA Marshall enable testing at ultra-high temperatures ($T < 2750\text{ }^{\circ}\text{C}$, 3023 K) with flowing ultra-high purity hydrogen. During this project, the heating assembly internal to the furnace was updated to eliminate coupling of the induction coil with the samples, which previously was predicted to result in large temperature gradients. In the updated design, CFEET uses inductive heating of a tungsten susceptor to quickly heat samples to temperatures exceeding $2750\text{ }^{\circ}\text{C}$. Temperature ramp rates of 50 – 400 K/min (1 – 7 K/s) have been demonstrated. Hydrogen flow rates can be varied between 500 – 1000+ standard cubic centimeters per minute (sccm), 0.500 – 1.00 standard liters per minute (SLPM), at atmospheric pressure. During testing, sample temperature, chamber pressure, gas flowrate, mixed outlet gas temperature, and power parameters (current, voltage, frequency, power) are monitored using an Agilent data acquisition system.

Prior to the experiments, the heating assembly and sample holder design was optimized to allow for high temperature operation, limited process gas contamination, and chemical compatibility with relevant components [93]. This effort is briefly summarized in Appendix D. To heat samples, an alternating electric current is supplied to the copper coil via a SP-16 50 kW power supply at a frequency of ~45 kHz to reach susceptor temperatures in excess of $2800\text{ }^{\circ}\text{C}$. The heating and sample holder assembly design is integrated and contained in a boron nitride (BN) electrical insulator that is placed on BN tubing to center the W susceptor in the coil and allow for hydrogen flow into the assembly. Since BN is not electrically conductive, it does not couple with the magnetic field produced during the induction heating and acts to insulate the susceptor against radiative heat losses to the enclosing water-cooled chamber walls. The insulator and susceptor are open to the top chamber window and have machined viewports at the axial centerline to allow for temperature measurements and in test video monitoring. Sample temperatures are recorded at the axial midline and top face using a Williamson Pro and Ircon Modline 5R 2-color pyrometer.

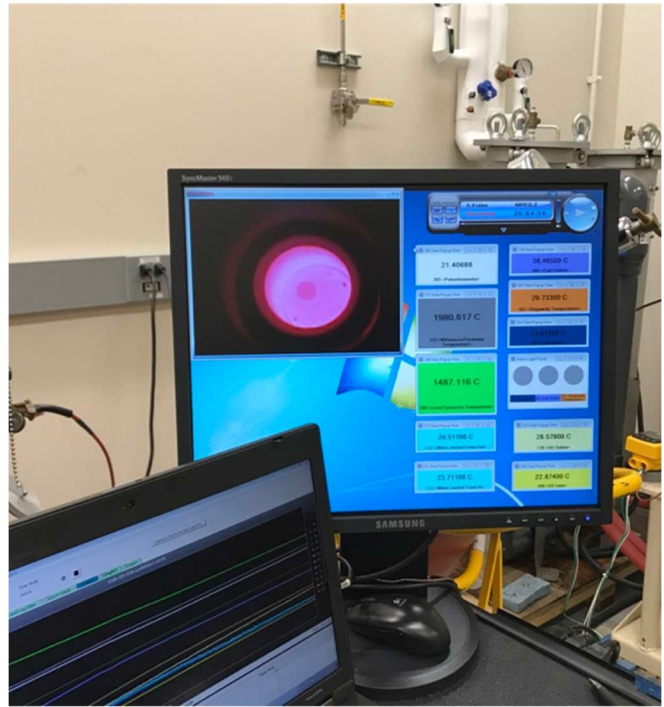


Figure 4.1 (Left) Compact Fuel Element Environmental Test (CFEET) Furnace and manual flow controls (Right) CFEET control panel and in-test monitoring of a sample during testing.

Current Capabilities

- Subscale fuel element testing: < 10 cm length, < 2.5 cm diameter
- Ultrahigh purity hydrogen gas flow
- Inductoheat SP-16 power supply
- Temperature Ramp Rates: 50 – 400 °C /min (1 – 5 K/s)
- 2+ hour steady state and thermal cycle testing
- dU/radioactive materials testing
- Maximum Temperature: 3000 K (anticipated)

In-Test Monitoring Equipment

- Ircon Modline® 5R two-color pyrometer (1000 – 3000 °C)
- Williamson PRO 80 two-color pyrometer (600 – 3000 °C)
- FAR FMP2/2X multispectral pyrometer (1200 – 4000 °C)
- MKS Flow Controller (volumetric flow rates: 450 – 1000 + sccm)
- Basler IP camera and recording for monitoring and post test investigation/trouble shooting
- Agilent DAQ system
- Hiden Analytical QGA Gas Analyzer

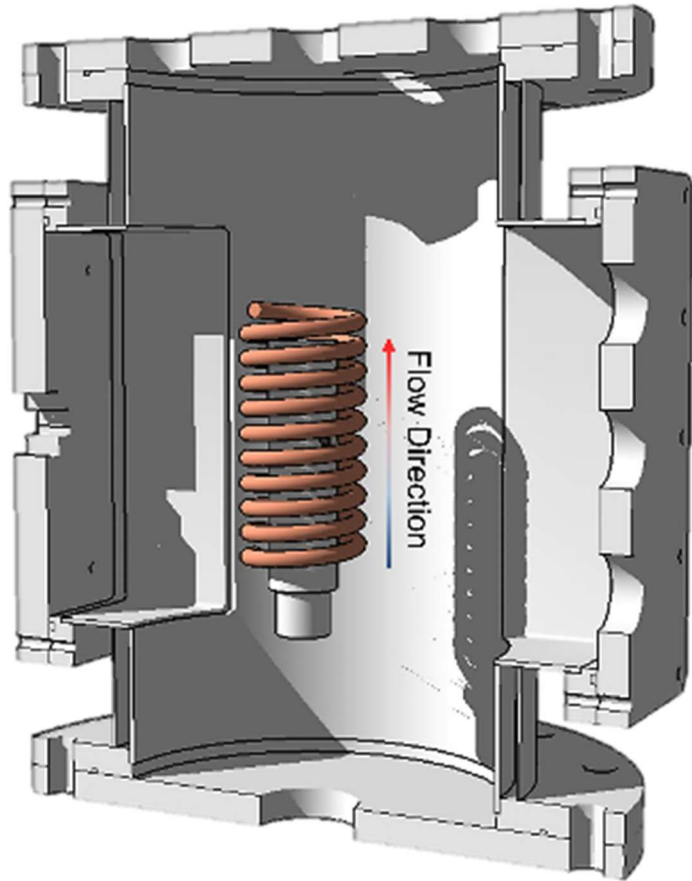


Figure 4.2 CFEET is a high temperature hydrogen induction furnace at NASA Marshall. An overview of current CFEET capabilities and in-test monitoring equipment available for testing is listed.

Pyrometers accuracy is reported by the manufacturers to be $\pm 0.25 - 0.5\% + 2.0\text{ }^{\circ}\text{C}$ and $\pm 0.5\% + 2.0\text{ }^{\circ}\text{C}$ respectively. Calibration of pyrometers was performed by melting high purity refractory metals (Zr, Hf, and Nb) and recording the observed temperatures upon sample melting.

The sample holder design is exhibited in figure 4.3. The material selection and design of the sample holder was optimized through chemical compatibility testing to allow for testing of carbon containing samples without interaction with the sample holder. Specimens are placed on a high purity plate of the tested carbide of interest (i.e. CVD SiC, TiC or ZrC) to prevent contamination of the sample during testing due to undesirable chemical interaction or unintentional suppression of the corrosion reaction due to interaction of from corrosion products produced downstream. Samples are axially and radially centered within the susceptor using a 0.5" diameter W bar. W is chosen because of its reported low vaporization rate at temperatures of interest and compatibility with hot hydrogen [24]. Preliminary testing during this thesis research demonstrated SiC is not compatible with W or BN at temperatures exceeding 2000 K. However, for temperatures up to 2750 K (2477 $^{\circ}\text{C}$), ZrC has been shown to exhibit acceptable compatibility with W and SiC for test temperatures/durations of interest (up to 45 minutes per thermal cycle) and was chosen as the material for a compatibility plate to allow for testing of SiC samples with the W centering bar.

While CFEET allows for sample temperatures of interest to NTP in flowing hydrogen to be achieved, the current set up operates at low flow rates, less than 1.00 standard liters per minute (SLPM) H_2 , and atmospheric pressure. True prototypic pressures and flow rates of the NTR cannot be achieved and are beyond the scope of this investigation, but would be suggested as a future research topic. CFEET qualification up to 2900 K (2623 $^{\circ}\text{C}$) is desirable to support NASA's NTP program's FY19/20 research. It is expected that the maximum achievable sample temperatures in the current configuration of CFEET will be limited to 2750 K to prevent rapid chemical interaction of the BN insulator and W susceptor. For scoping of novel fuel forms capable of ultrahigh temperatures ($T > 3000\text{ K}$), induction furnace design remains to be developed. Another current limitation of the CFEET system includes continuous, low achievable flow rates of hydrogen during testing. Due to the sizing of the outlet gas fume vent and mass flow controller capabilities, flow rates are limited to 1 SLPM or less. While reported exposure times only includes steady state hold time at the target temperature, continuous gas flow during furnace operation results in added mass change during the temperature ramp up and ramp down process. To reduce the impact of this effect, ramp rates were set to 400 $^{\circ}\text{C}/\text{min}$. A sample thermal cycle temperature profile is shown in figure 4.4.

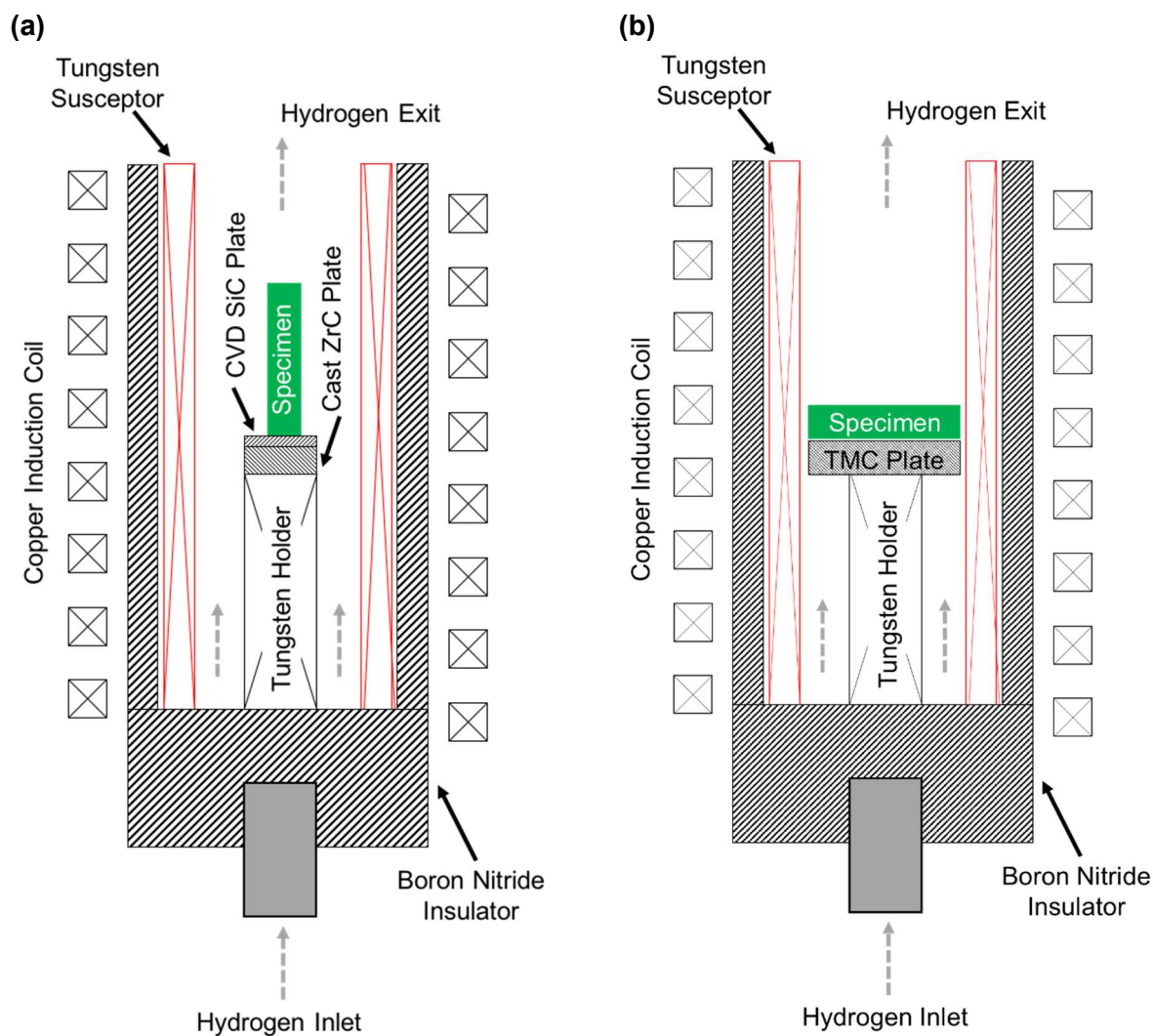


Figure 4.3 Schematic drawing of CFEET heating assembly and flow path, detailing the W centering bar and (a) ZrC compatibility plate, and SiC sample holder plate for SiC samples and (b) TMC compatibility plate and TMC specimens for TMC samples

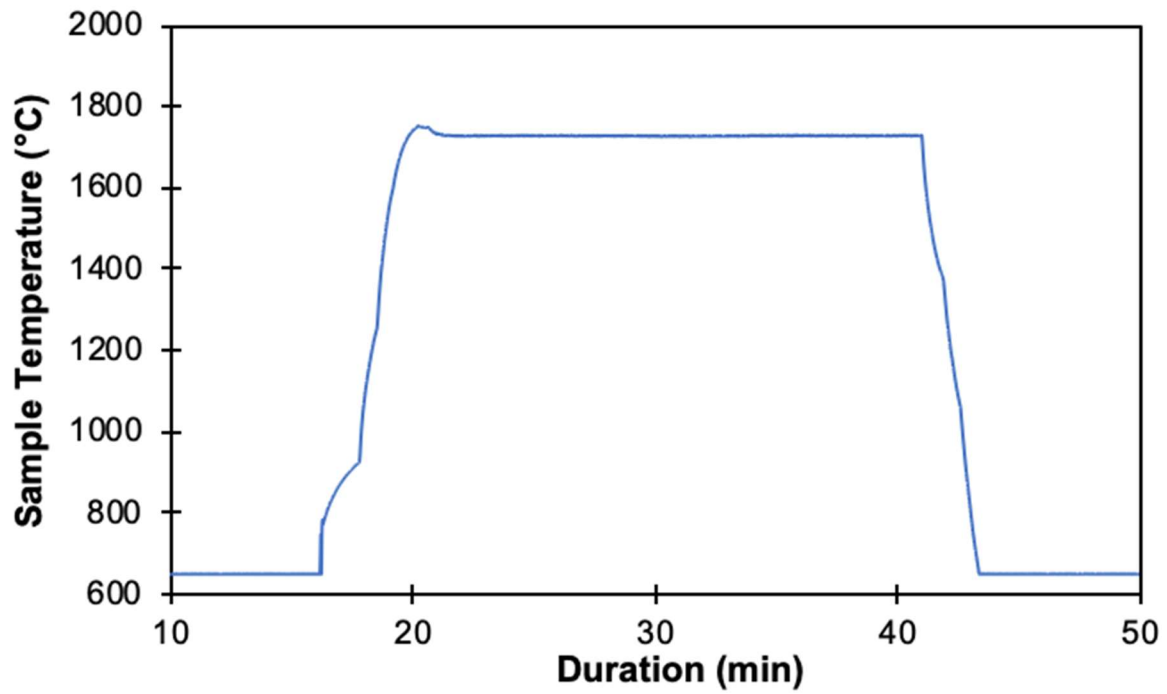


Figure 4.4 Example sample test temperature profile for a 2000 K thermal cycle. Ramp up to full temperature is 400 °C/min, ramp down is approximately 450 °C/min.

Experimental Objectives

Intrinsic stability of SiC in hydrogen

To evaluate the intrinsic stability of SiC in a hydrogen environment, high purity, near theoretical density CVD β -SiC sample coupons were thermal cycled in ultra-high purity hydrogen gas. The volatilization behavior of SiC was evaluated by probing the time, gas velocity, and temperature dependence of SiC mass loss behavior in flowing hydrogen. Thermal cycling at temperatures of 2000, 2250, and 2500 K were completed to evaluate the time dependence of mass loss rate and evaluate the apparent activation energy at very high temperatures. Velocity testing was completed at 2000 K for gas velocities of 12, 18, 24 cm/s to evaluate if mass loss was surface reaction limited or mass transfer limited. Mass change measurements were coupled with microstructural characterization to determine rate limiting corrosion mechanisms, evaluate relevant corrosion products, and assess bulk microstructural stability of silicon carbide.

Investigation of NITE silicon carbide performance in hot hydrogen and identification of the impact of sintering additives

In this study, NITE SiC was subjected to low temperature duration testing and high temperature thermal cycle testing in flowing hydrogen to compare the performance of as fabricated NITE SiC to intrinsic SiC testing. High temperature thermal cycle testing was completed for exposure temperatures of and 2000, 2250, and 2500 K for 30 – 120 minutes. Additional investigation of NITE SiC stability was evaluated through low temperature duration testing. NITE SiC sample rods were tested at temperatures of 1173, 1373, 1573, 1773, and 1973 K for up to 120 minutes to evaluate the apparent activation energy of NITE SiC. The mass loss behavior of NITE SiC was compared to that of high purity CVD SiC and the microstructure was evaluated to determine degradation mechanisms and impact of oxide additive eutectics on the performance and stability of NITE SiC in NTP relevant environments.

Intrinsic Stability of TMCs in hydrogen

The intrinsic stability of TiC and ZrC in hydrogen was evaluated through thermal cycle and velocity testing. The volatilization behavior of the TMCs was evaluated by probing the time, gas velocity, and temperature dependence of TMC mass loss behavior in flowing hydrogen. Sample rods of TiC and high-density sample plates of TiC and ZrC were thermal cycled at temperatures of 2000, 2250, and 2500 K were completed to evaluate the time dependence of mass loss rate and

evaluate the apparent activation energy at very high temperatures. Velocity testing was completed at 2000 K for gas velocities of 12.06, 18.09, 24.12 cm/s to evaluate if mass loss was surface reaction limited or mass transfer limited. Mass change measurements were coupled with microstructural characterization to determine rate limiting corrosion mechanisms, evaluate relevant corrosion products, and assess bulk microstructural stability of refractory carbide materials of interest.

Materials

Silicon Carbide

Plates of near theoretical density, high purity (>99.99%) β -SiC formed via chemical vapor deposition (CVD) were supplied by Oak Ridge National Laboratory. It was desired to a form of SiC that was near theoretical density and high purity to in order study intrinsic corrosion response and limit the effects of porosity and impurities on observed kinetic behavior. For thermal cycling and velocity testing, plates were machined into 6 mm diameter, 25 mm long sample pins. Discs of hot pressed-NITE SiC containing 6 wt% Y_2O_3 and Al_2O_3 oxide additives were supplied for testing by Oak Ridge National Laboratory. For very high temperature thermal cycling tests (2000 – 2500 K), cylindrical sample pins of 25 mm length and 6 mm diameter were machined for hot hydrogen exposure testing. For low temperature duration testing (973 – 1973 K), square sample rods of 25 mm length and 6 mm thickness were machined. Prior to testing, sample surface finish was left as the as machined finish for cylindrical surfaces and all flat exposed surfaces were polished to a 1 μ m finish using diamond lap films, samples were ultra-sonicated in an acetone bath, dried, measured with calipers, and weighed using an analytical balance.

Transition Metal Carbides

Initial scoping studies were completed using TiC sample pins of 6 mm diameter, 25 mm length (99.97% purity, metals basis) procured from American Elements. Ultimately it was determined the high porosity of procured TiC samples were undesirable to determine the intrinsic corrosive response of TiC due to impact of porosity on observed weight change. ZrC and TiC samples for testing were sintered using spark plasma sintering (SPS) at NASA Marshall Spaceflight Center. SPS parameters were based upon sintering conditions previously optimized for sintering of near theoretical density mixed VC-ZrC-NbC billets [94]. Blended powders were sintered into 20 mm diameter, 3 mm thick sample plates using SPS parameters of 1800 °C, 50 MPa, 30-minute dwell time to ensure a near theoretical density pellet with a low porosity was fabricated. Fabricated

sample density was assessed as acceptable as long as porosity was present as closed porosity only (> 96% TD). After sintering, samples were prepped for testing by grinding flat with silicon carbide paper until the protective grafoil® on the sample faces was removed. Following grinding, samples were polished to 1 µm finish using diamond lap film. Following polishing, samples were cleaned with deionized water, degassed in ethanol, dried, measured, and weighed using a precision balance. Prepared samples were transferred and loaded into CFEET for 2000 and 2250 K thermal cycling up to 120 minutes duration in flowing H₂.

Standard Testing Conditions and Procedures

All experiments were completed at NASA Marshall Space Flight Center using the compact fuel element environmental test (CFEET) furnace described previously. Prior to testing, samples were cleaned with deionized water, degassed in ethanol, dried, measured, and weighed using a Mettler Toledo XP analytical balance. Three axially equidistant diametric measurements and overall sample length was measured using calipers. Prepared samples were transferred and loaded into CFEET for high temperature, flowing H₂ exposure. SiC samples were placed upon a CVD SiC sample plate and centered within the heating assembly using a W centering rod, a ZrC compatibility plate separated the SiC sample plate and W centering rod, schematic drawing shown in figure 4.3. TMC samples were placed upon a plate of the same material and centered within the heating assembly using a W centering rod.

For standard thermal cycling conditions, standard H₂ conditions regulate mass flow rate of hydrogen into the furnace at a rate of 0.500 standard liters per minute (SLPM) throughout the duration of testing, including heating and cooling. Samples are ramped to temperature at a rate of ~400 °C/minute, held at temperature for the desired duration, and subsequently ramped down to room temperature at a rate of ~400 °C/minute using manual control of the power supplied to the induction furnace. Sample temperature measured using a Williamson Pro 2-color pyrometer and Ircon Modline 2-color pyrometer with respective ranges between 650 – 2800 °C (923 - 3073 K), 1000 - 2500 °C (1273 – 2773 K). The maximum observable sample temperature was taken as the steady state test temperature; the temperature was manually controlled through control of input power to the coil in order to retain observable sample temperature to less than ± 10 °C deviation in hold temperature throughout testing. Cool down rate is limited by convection once zero power is achieved and an argon purge is utilized to cool the sample to room temperature for removal and inspection. During velocity testing, H₂ inlet flow rate is varied at 0.500, 0.750, 1.000

SLPM in order to achieve gas flow velocities of 12.06, 18.09, 24.12 cm/s within the heating assembly (assuming full expansion of the hydrogen gas at test temperature).

After each thermal cycle, all samples were weighed and characteristic sample dimensions were measured. Once thermal cycling or testing was completed, cylindrical sample rods were prepared for microstructural characterization. The exposed sample top face and axial midsection was cross sectioned from the sample and internal surfaces ground flat to ~4000 grit silicon carbide paper to form 6 mm diameter, 2 mm thin button samples for x-ray diffraction (XRD), optical microscopy (OM), scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDS), and Raman micro-spectroscopy analysis. TMC sample plates did not require additional sample preparation after testing. XRD measurements are performed to assess the overall compositional stability of the near surface region (top face sample) and bulk microstructure (midsection sample). OM, SEM, and EDS analysis is performed to characterize corrosive attack to the exposed sample microstructure and identify relevant corrosion products. Raman spectroscopy is performed to identify the phase/structure of corrosion products.

CHAPTER FIVE - RESULTS AND DISCUSSION

Intrinsic stability of SiC in hydrogen

Observed Corrosion Kinetics of CVD SiC in Flowing Hydrogen

Thermal cycling of CVD β -SiC was completed at temperatures of 2000 and 2250 K up to 120 minutes. A sample pin was tested for one thermal cycle at 2473 K for 30 minutes, which resulted in significant enough mass loss to prevent further thermal cycling. At temperatures of 2000 and 2250 K, exposed samples exhibited relatively uniform recession across the sample length and visual examination allowed for the identification of the formation of corrosion products on the surface after exposure. Typical surface microstructures of CVD SiC after exposure are exhibited in figures 5.1, 5.2, and 5.3. In these micrographs a mix of grain boundary etching and corrosion product formation at the grain boundaries or in large condensate bubbles are present. At 2250 K, condensate bubbles are present in less frequency and striations across the grains indicate that corrosion is enhanced through intergranular attack of the exposed SiC grains. At the highest test temperatures, no corrosion products are evident and the surface microstructure exhibits extensive etching and grain boundary attack.

Raman spectroscopy was used to identify the composition and structure of the exposed microstructure. A 473 nm wavelength laser at 12.5 mW power was used to avoid resonances that obscure measurement of the surface microstructure and provide a strong enough signal to see the first and second order spectra of the bulk microstructure and relevant corrosion products for phase identification. Shown in figure 5.4 is the characteristic Raman spectra of representative CVD SiC microstructures exposed to 2000 K flowing hydrogen. The bulk microstructure was found to retain a primarily β -SiC structure with characteristic transverse and longitudinal optic (TO and LO) peaks at 795 and 970 cm^{-1} . Small peaks between 1500 – 1700 cm^{-1} and at 510 cm^{-1} correspond to the second order Raman spectra β -SiC and the formation of free Si present on the surface and grain boundaries of SiC. The Si rich condensate features contain a Si structure with characteristic first and second order peaks at 510 and 970 cm^{-1} when probed with Raman microanalysis. The lack of broadening of the first order Si peak indicates that the condensate does form a crystalline structure upon cooling, rather than an amorphous form of free Si.

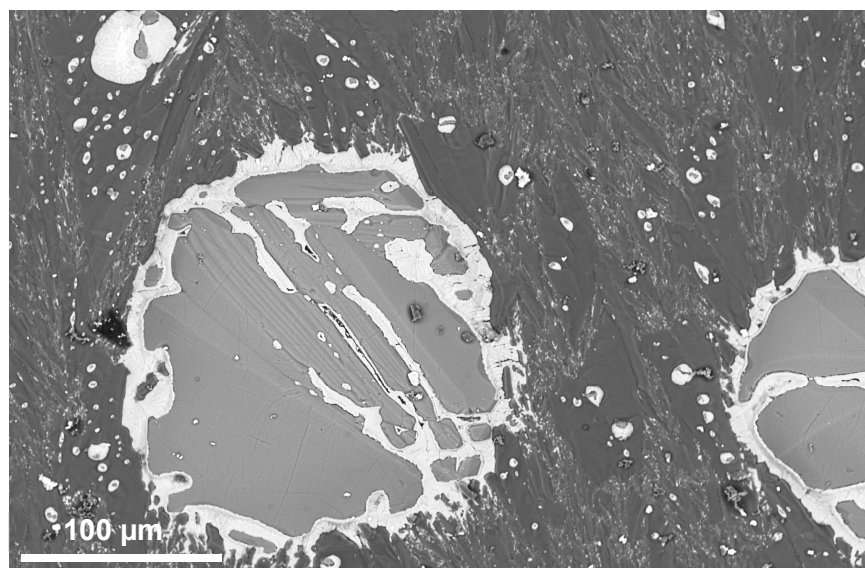
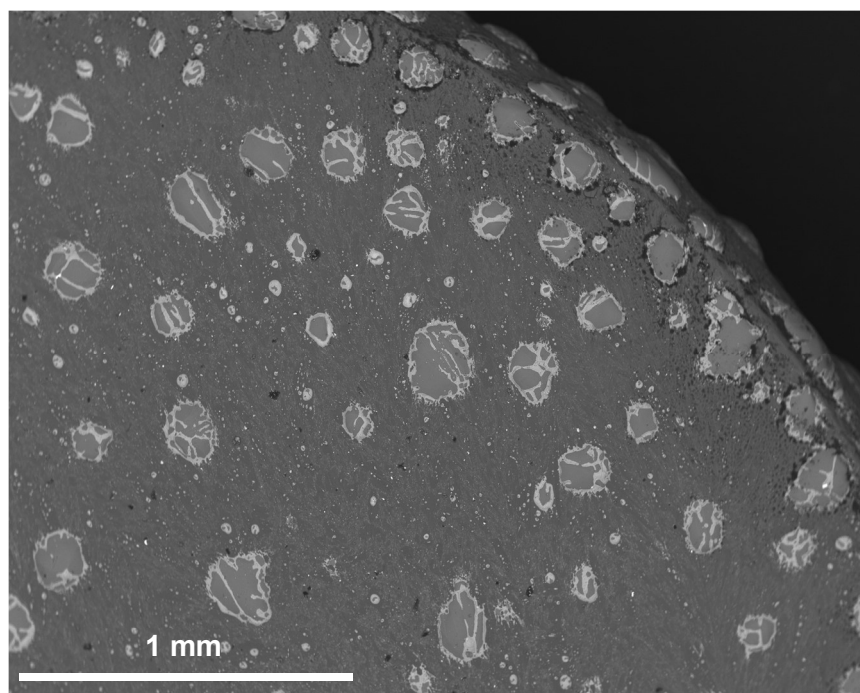


Figure 5.1 Backscatter electron (BSE) images of CVD SiC exposed to hot flowing hydrogen at 2000 K for 120 minutes showing compositional contrast of the bulk material and relevant corrosion products.

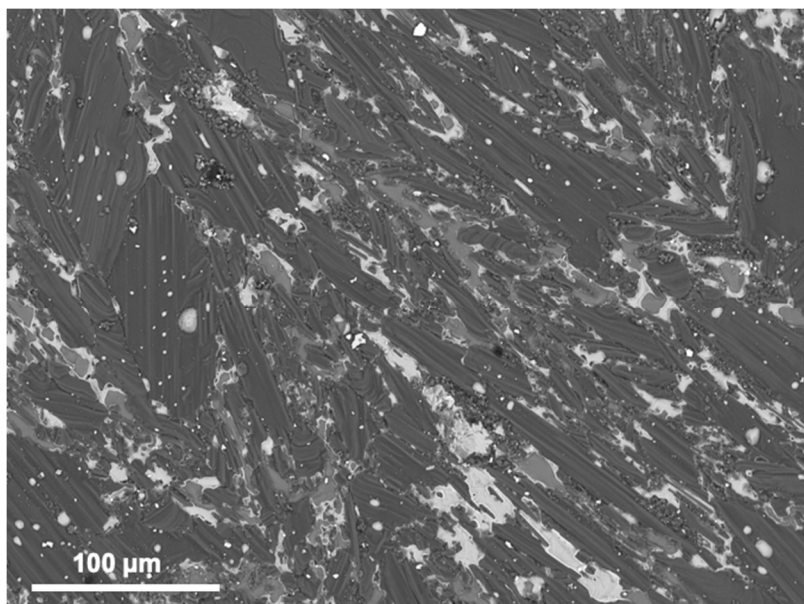
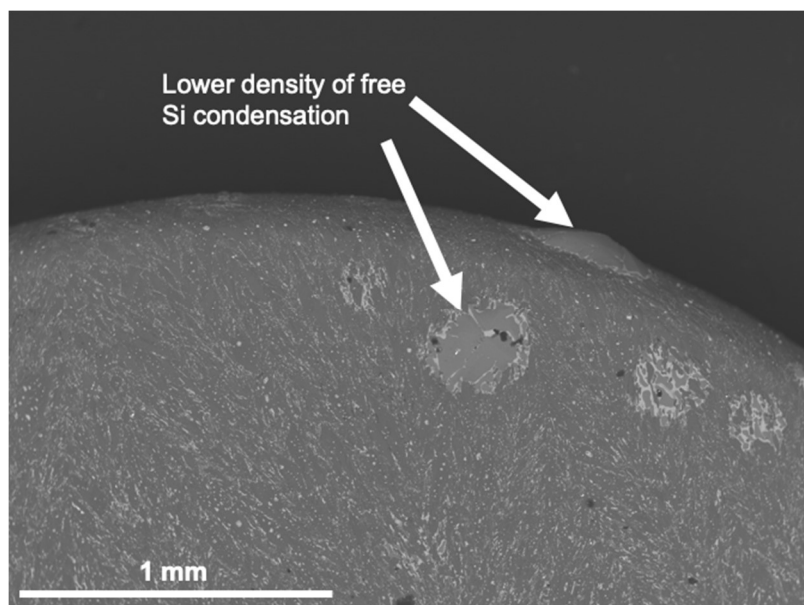


Figure 5.2 BSE images of CVD SiC exposed to hot flowing hydrogen at 2250 K for 120 minutes.

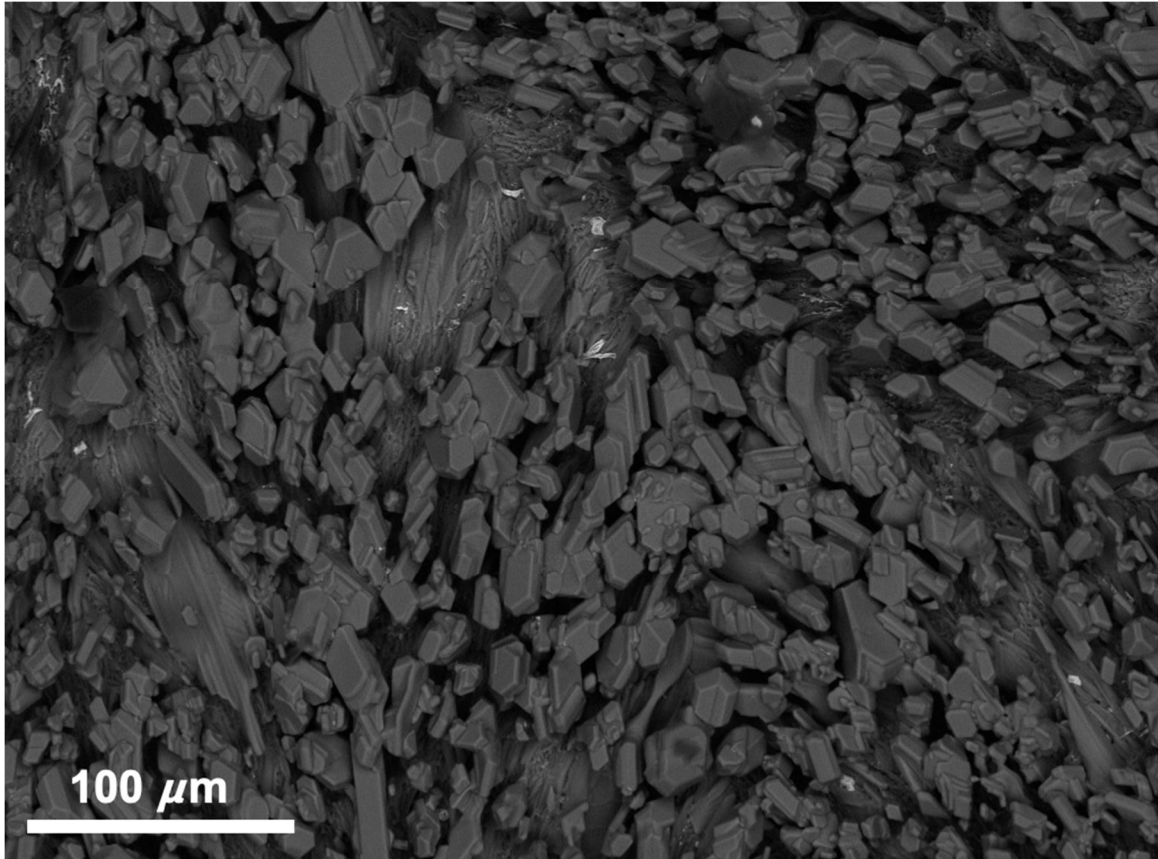


Figure 5.3 BSE images of CVD SiC showing typical microstructures after exposure to hydrogen at temperatures exceeding 2250 K. Significant grain etching of the entire microstructure occurs.

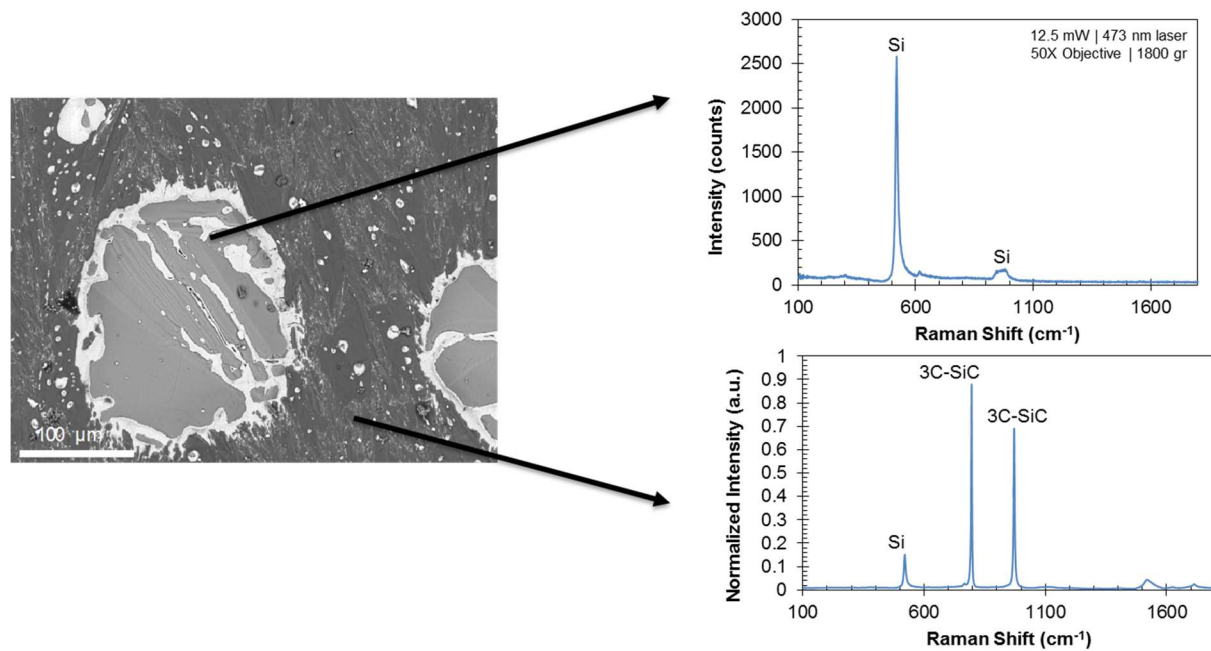


Figure 5.4 Representative Raman spectra of the bulk exposed microstructure and observed corrosion products of CVD SiC exposed to flowing hydrogen at 2000 K for 120 minutes.

Weight change of CVD SiC samples thermal cycled in flowing hydrogen at temperatures of 2000, 2250, and 2473 K is shown in figure 5.5. No weight gain was observed for any of the samples and observed mass losses exhibited a linear dependence with increasing exposure duration at 2000 and 2250 K. From the microstructural analysis, at 2000 K, etching of SiC samples surfaces is primarily driven by grain boundary attack, while at 2250 K, SiC samples corrode by a mix of grain boundary attack and intragranular grain etching. At 2500 K, complete etching of the entire exposed surface microstructure occurs to promote rapid mass loss of SiC. Free Si is the primary observed corrosion product and all exposures were completed at temperatures above the melting point of Si (~1687 K).

While, free Si is the primary corrosion product and is originally formed as a liquid phase on the surface, it is not observed to passivate the surface from hydrogen attack. In the case of passivating corrosion, a parabolic trend of corrosive mass change with exposure temperature is expected due to formation of a stable, nonreactive, protective corrosion product on the sample surface, which slows further weight change. Both the microstructural analysis and observed corrosion kinetics are consistent with volatilization of gas phase corrosion products governing corrosion rate. When formed during the very high exposure temperatures, free Si is stable in the liquid phase; however, it can vaporize to leaves the surface as volatile Si_(g) into the gas stream rather than form a passivating layer. The decreasing prevalence of free Si with increasing exposure temperature could point to its decreasing stability as a liquid phase on the sample surface with temperature. In this study, the linearity of increasing mass loss with exposure duration indicates that corrosion rate is not dependent upon any intermediate step of forming a solid corrosion product on the surface of the samples. From the weight change trend, mass loss is primarily limited by direct formation of volatile corrosion products and their subsequent loss from the surface. For volatilization corrosion kinetics, the mass transfer coefficient (h) can be described with a linear rate constant (k_L), as shown in equation 5.1:

$$h = k_L(C_s - C_\infty) \quad (\text{Eq. 5.1})$$

k_L – linear rate constant C_s – gas species concentration at the surface C_∞ – gas species concentration in the gas stream far from the surface

Therefore, the time dependence of weight change is simply (Eq. 5.2):

$$\Delta w = ht = k_L t \quad (\text{Eq. 5.2})$$

Δw – observed weight change h – mass transfer coefficient k_L – rate constant t – time

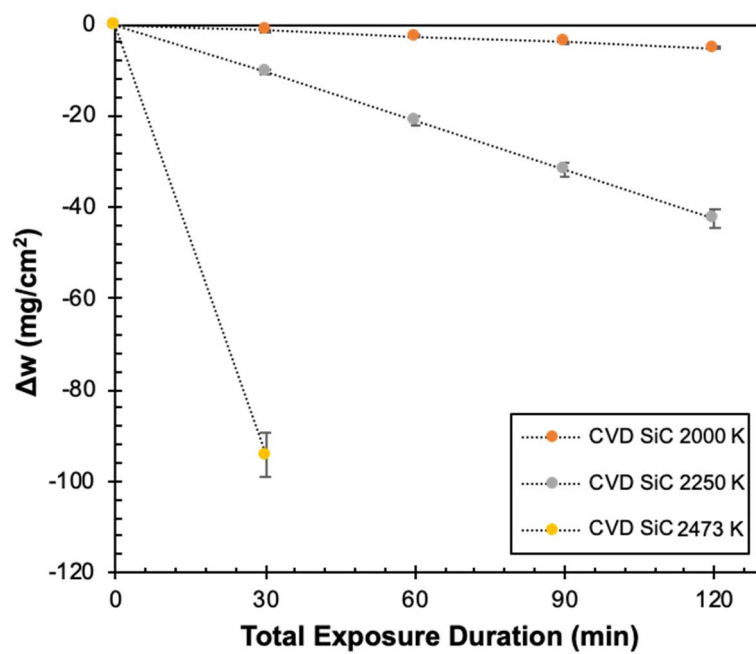


Figure 5.5 Observed mass change behavior of CVD SiC in flowing hydrogen (12 cm/s).

The linear volatilization rate constant (k_L) was derived for each thermal cycle data set as simply the slope of observed mass loss with exposure duration. For 2000 and 2250 K exposure temperatures, rates of mass loss were high, but acceptable for NTP applications, with an average linear rate constant of 2.6 and 21 mg/cm²hr for 2000 and 2250 K runs respectively. Measured SiC mass loss rates exceeded historically observed midband corrosion maxima at temperatures of 2250 K and greater. At the highest temperature exposure, 2473 K, mass loss rates were too excessive ($k_L = 190$ mg/cm²hr) for use in NTP applications. Measured SiC rate constants increased exponentially with increasing exposure temperature. Figure 5.6 shows the logarithmic dependence of derived rate constants of CVD SiC with temperature. The Arrhenius dependence of the rate constant on exposure temperature allowed for the determination of the apparent activation energy by fitting the curve with the trend (Eq. 5.3):

$$k_L = A \cdot \exp\left(-\frac{E_A}{RT}\right) \quad (\text{Eq. 5.3})$$

k_L – rate constant A – pre-exponential constant E_A – apparent activation energy

R – gas constant (8.314 J/molK) T – temperature

The slope of the logarithmic dependence of the rate constant on inverse temperature can be related to the apparent activation energy (E_A) by the gas constant (Eq. 5.4):

$$E_A = -mR \quad (\text{Eq. 5.4})$$

E_A – apparent activation energy m – slope R – gas constant (8.314 J/molK)

The preceding analysis resulted in a determination of apparent activation energy of 370 +/- 18 kJ/mol.

The limiting step of the loss of volatile gas species from the surface is either surface reaction controlled or mass transfer controlled. In the mass transfer-controlled process, the diffusion of the volatile reaction products through the boundary layer limits the corrosion rate for etching of the surface microstructure, this rate is dependent upon the gas stream properties which govern the mass transport coefficient. Where as in a surface reaction controlled process, mass loss is independent of the rate of convective mass transfer. In order to evaluate whether the limiting corrosion step for SiC was controlled via surface reaction or mass transfer, samples were tested for 30 minutes at 2000 K with varying gas velocities. Gas velocity was controlled through the mass

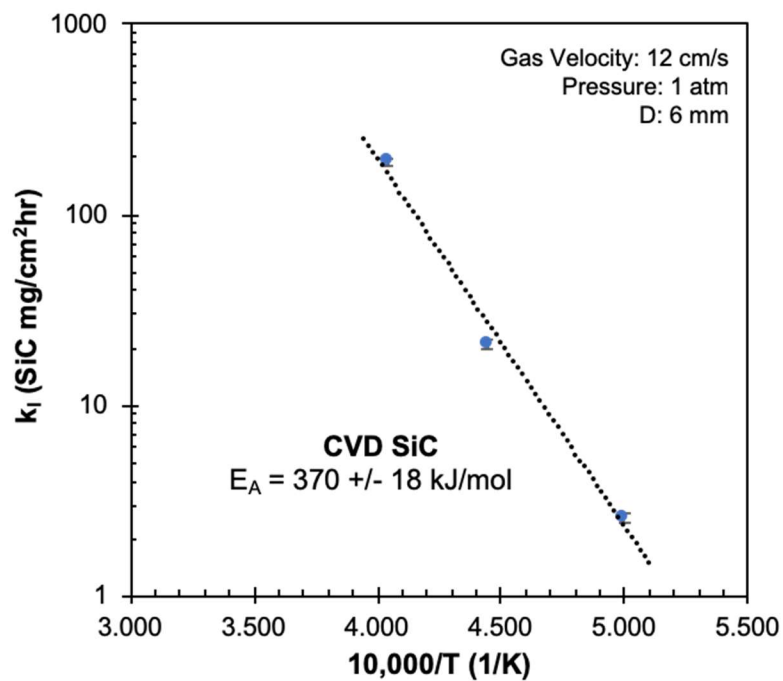


Figure 5.6 Temperature dependence the linear rate constant derived from CVD SiC volatilization in flowing hydrogen.

flow rate allowed into the furnace, velocities of 12, 18, and 24 cm/s were calculated to correspond to increasing the mass flow rate of hydrogen into the furnace at a rate of 500, 750, and 1000 sccm. Sample weight change dependence on gas velocity is shown in figure 5.7. Overall, samples experienced a great increase in mass loss rate with gas velocity. For velocities of 12 and 24 cm/s, mass loss rates increased by more than two-fold from 2.6 to 6.2 mg/cm²hr. Optical micrographs of CVD SiC corroded under varying gas velocities show free Si condensation is no longer as prevalent on the surface for gas velocities of 18 cm/s and greater (figure 5.8). As gas velocity increases, while no large condensate is evident, increased etching of exposed SiC grains is observed. The trend of increasing mass loss with increasing gas stream velocity is consistent with mass transfer limited process.

Comparison of Observed SiC Corrosion to the Boundary Layer Diffusion Model

CVD SiC was observed to uniformly corrode through the etching of SiC and formation of volatile gas species during high temperature hydrogen exposure (2000 – 2500 K). Mass loss of CVD SiC exhibited an Arrhenius temperature dependence and direct dependence upon gas stream velocity. This behavior consistent with the limiting corrosion step governed by gas transport of volatile species through the boundary layer. As previously discussed, in the boundary layer limited diffusion model, the mass transfer coefficient is directly related to the Sherwood number and corrosion product diffusivity, both of which are dependent on the properties of the gas stream, i.e. gas density, viscosity, temperature, pressure (Eq. 5.5):

$$h = Sh \frac{D}{L} = f(Re, Sc) \quad (\text{Eq. 5.5})$$

h – mass transfer coefficient D – diffusion coefficient L – characteristic length
 Re – Reynold's number Sc – Schmidt number

For a long cylindrical rod in axial flow, solution of the heat transfer coefficient (h) through the Sherwood number was selected to follow the correlation (Eq. 5.6):

$$Sh = 0.700 Re^{\frac{1}{2}} Sc^{\frac{1}{3}} \propto v^{\frac{1}{2}} \quad (\text{Eq. 5.6})$$

The derived temperature dependent linear rate constants for CVD SiC under standard test conditions (1 atm pressure, 12 cm/s gas velocity) is compared to predicted mass losses of SiC for different volatile species in figure 5.9. Similarly, in figure 5.10, predicted SiC mass loss rates for varying gas velocities is compared to experimentally determined values. Overall, the apparent activation energy of CVD SiC (370 kJ/mol) which best agrees with vaporization of volatile Si

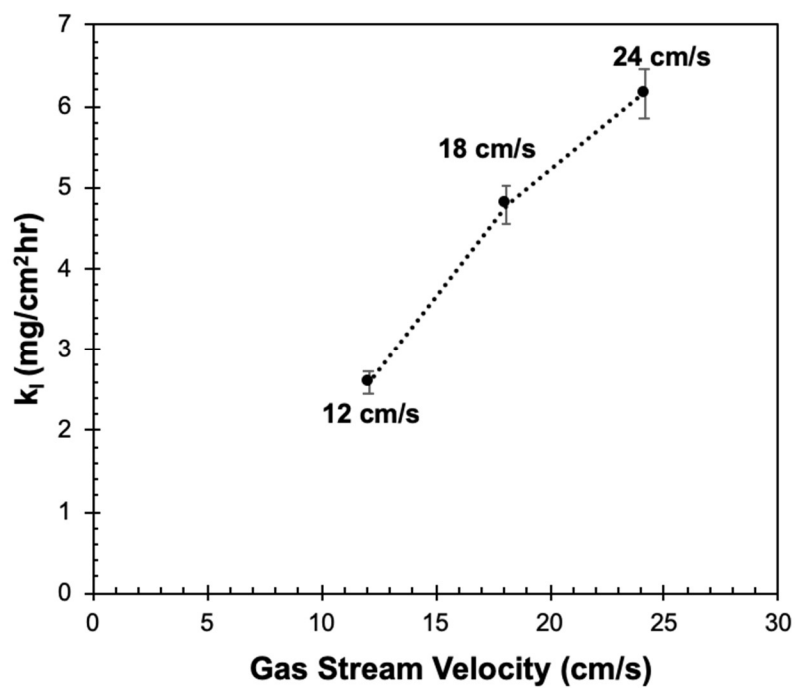


Figure 5.7 Observed mass loss rate of CVD SiC in flowing hydrogen at 2000 K. Mass loss rate increases with increasing flow velocity.

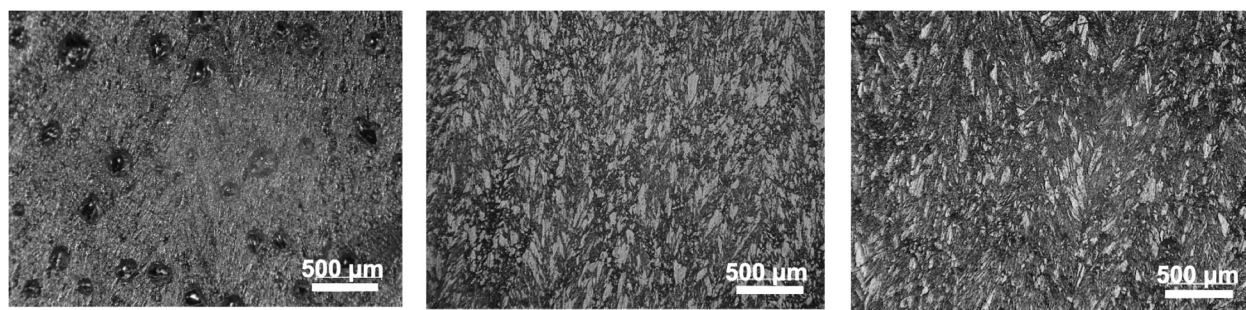


Figure 5.8 Optical micrographs of CVD SiC subjected flowing hydrogen at 2000 K at a flow velocity of (a) 12 cm/s, (b) 18 cm/s and (c) 24 cm/s.

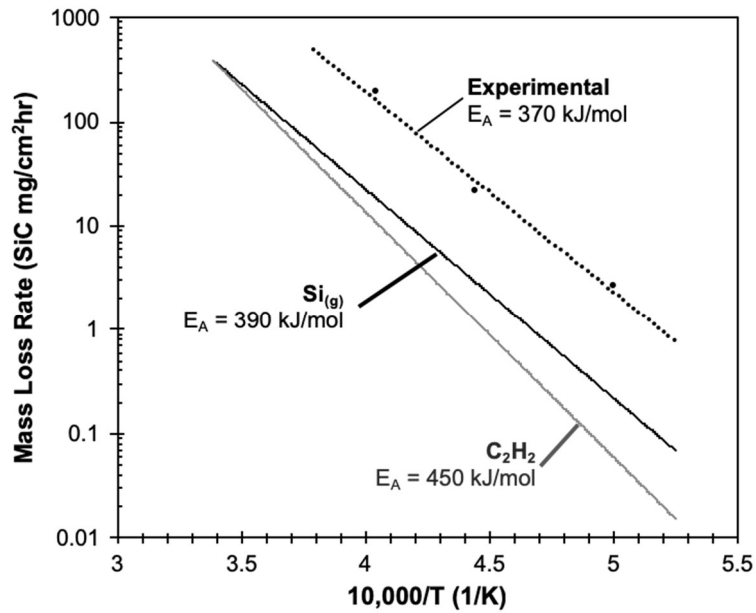


Figure 5.9 Comparison of the temperature dependence of experimentally observed and predicted mass loss rates of SiC using the boundary layer diffusion gas transport model.

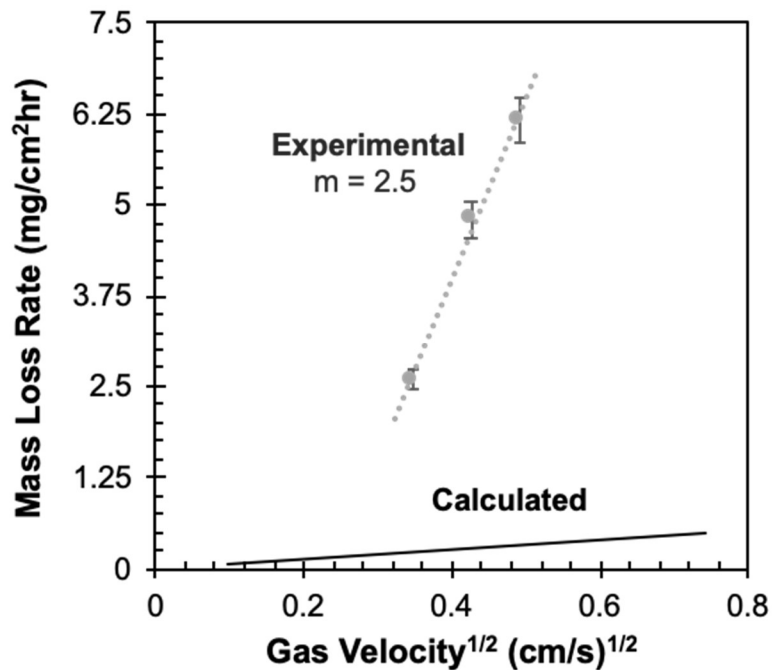


Figure 5.10 Comparison of the velocity dependence of experimentally observed and predicted mass loss rates of SiC using the boundary layer diffusion gas transport model.

(390 kJ/mol). However, experimentally determined mass losses were an order of magnitude higher than predicted values. Additionally, predicted change in mass loss rate with gas velocity was much lower than experimentally measured. A dependence of SiC mass loss rate was anticipated to scale with the $\frac{1}{2}$ power of gas stream velocity due to the selected correlation for the Sherwood number. When plotting experimental data with respect to the square root of velocity, the experimental values appeared to exhibit a linear dependence with $v^{1/2}$, however mass loss increased at a higher rate than predicted with the Sherwood number, and the predicted intercept of the mass loss rate was nonzero.

Discussion of Results

CVD SiC corroded via volatilization reaction in hot hydrogen, free Si was the primary corrosion product evident on the surface. Weight change behavior exhibited a linear dependence with exposure duration and a strong dependence on gas flow rate, which is consistent with mass transfer limited volatilization process with no passivating corrosion product formation. The apparent activation energy of SiC volatilization in hot hydrogen was experimentally determined to be 370 kJ/mol. Comparing experimental results to analytical calculations of predicted mass loss rates using boundary layer theory, free Si vaporization (390 kJ/mol) from the surface was identified as the controlling step for SiC corrosion in hot hydrogen.

Predicted values were in good agreement with experimental observations. There was an order of magnitude difference of predicted and experimental values for standard test conditions. This difference increased with increasing gas flow velocity. This relationship may suggest that the assumed correlations for the mass transfer coefficient used in analytically predicting mass loss rates from boundary layer theory may be the primary source of error. In more detailed studies, comparison of the heat transfer and mass transfer correlations, dependent upon furnace/sample geometry and resulting effect on gas flow distribution, should be conducted to identify the best correlation for the Sherwood number to predict the mass transfer coefficient. Other sources of error may be due to selection of gas transport properties, such as temperature, density or viscosity. Selection of proper gas film properties may enable greater agreement between predicted and experimental values.

Compared to acceptable mass loss following midband corrosion in historic NTP graphite composite fuels CVD SiC corrosion performance was acceptable for temperatures up to ~2150 K in flowing hydrogen. However, for mass transfer limited processes, gas flow parameters of pressure and velocity are known to directly correlate with the mass transfer coefficient, suggesting

much higher mass loss may be expected under prototypic use conditions. This high apparent activation energy of CVD SiC in hot hydrogen suggests that mass loss rates of SiC will be acceptably low for the mid-band and inlet fuel regions of an NTP engine. CVD SiC may be an alternative coating material to reduce high mass losses seen previously for the mid-band region due to low reactivity with hydrogen as well as anticipated chemical compatibility and reduced incurred thermal stresses caused by mismatch in the coefficient of thermal expansion compared to alternative refractory carbides. Future studies should probe the dependence of observed mass loss rate on exposure pressure and temperature.

Investigation of NITE Silicon Carbide Performance in Hot Hydrogen and Identification of the Impact of Sintering Additives

The fabrication route for engineering scale SiC-based components for nuclear energy applications has been demonstrated using the nano-infiltration transient eutectic (NITE) fabrication technique. This technique uses nano-dispersed alumina rare earth oxide additives such as Y_2O_3 and Al_2O_3 to form a high melting temperature eutectic with the SiC matrix to reduce powder sintering process conditions required for hot pressing or spark plasma sintering methods. This process results in a high density carbide matrix with a dispersion of residual, partially glassy eutectic compounds throughout the microstructure [58]. NITE allows for a reduction in process temperatures and pressures required to form high density, net shape components, compared to alternative SiC sintering techniques, which is advantageous for sintering of large-scale components or fully ceramic microencapsulated (FCM) fuels. Specific to FCM fuels, NITE fabrication processes allows for sintering of SiC matrix composite fuel forms at the low enough temperatures and pressures necessary for fabrication compatibility with the TRISO particle fuel design. In the previous section, the intrinsic stability of SiC was assessed via thermal cycling of high purity, near theoretical density β -SiC sample coupons. In this section, the results of NITE SiC corrosion kinetics and microstructural stability under conditions relevant to NTP are reported.

Observed Corrosion Kinetics of NITE SiC in Flowing Hydrogen

In this study, NITE SiC was subjected to low temperature duration testing and high temperature thermal cycle testing in flowing hydrogen. High temperature thermal cycle testing was completed for exposure temperatures of and 2000, 2250, and 2500 K for 30 – 120 minutes in order to investigate the corrosion kinetics of NITE SiC for comparison to intrinsic SiC performance. Low temperature duration testing was undertaken with NITE SiC sample rods at temperatures of 1173, 1373, 1573, 1773, and 1973 K for up to 120 minutes, to determine the stability of NITE SiC for a wide range of exposure temperatures relevant to NTP operation and identify different limiting corrosion regimes. In general, NITE SiC was much more susceptible to hydrogen attack than CVD SiC. Following exposure to hydrogen. Similar to CVD SiC, NITE SiC was only able to survive one thermal cycle at the highest exposure temperature due to extensive attack of the sample pin. Photographs of NITE SiC and CVD SiC sample pins following hot hydrogen thermal cycling at 2000 K and one thermal cycle at 2500, 2473 K respectively are showing in figure 5.11 Compared to CVD SiC, even visual examination shows the microstructure of NITE SiC is much more degraded following hydrogen attack. For 200 and 2250 K exposures, NITE SiC exhibited uniform

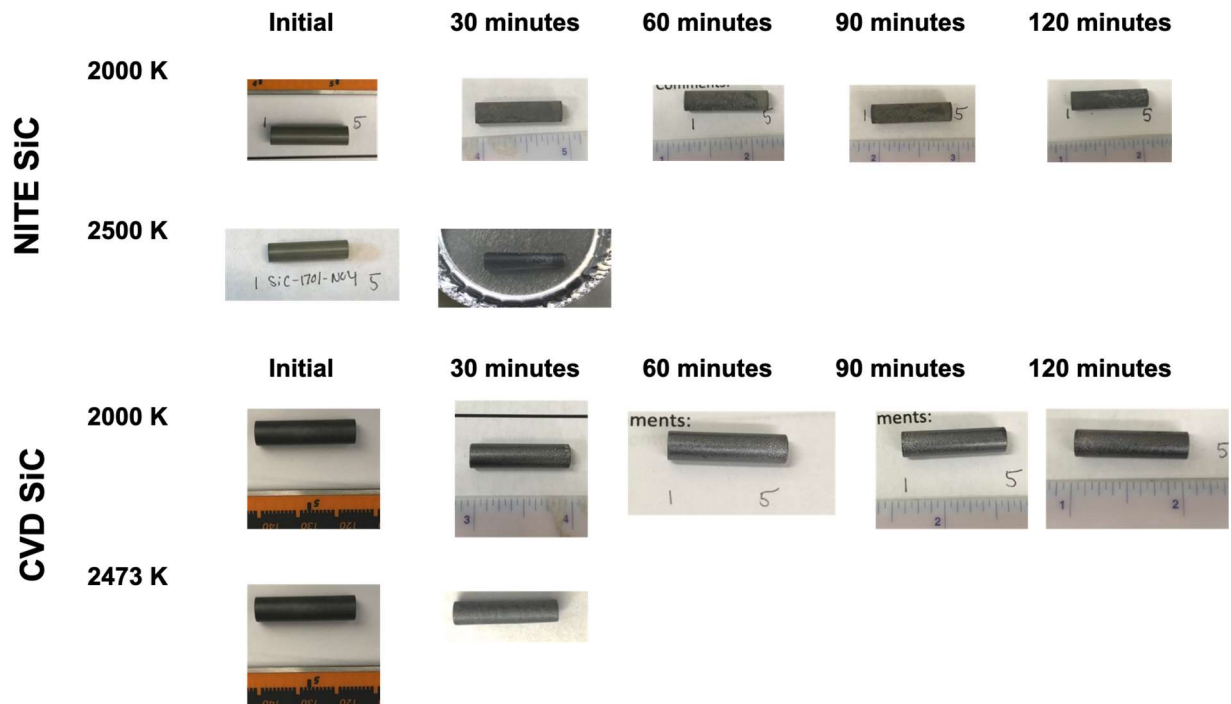


Figure 5.11 Images taken of NITE SiC (top) and CVD SiC (bottom) sample pins following exposure to thermal cycling at 2000 K and 30 minutes at ~2500 K

radial recession under flowing hydrogen conditions. At 2500 K, radial recession was most significant at the bottom of the sample corresponding to where the sample is seated in the sample holder assembly. This position corresponds to the region first exposed to the hydrogen gas. Non-uniform sample corrosion at this temperature may be indicative that corrosive mass losses are high enough to contaminate the gas stream to create a local gas composition, which suppresses downstream corrosion. In this case, absolute mass loss of NITE SiC in pure hydrogen at 2500 K may be greater than measured values. During testing of NITE SiC at 2500 K, corrosion rates were high enough to completely coat the upper viewport of the CFEET furnace (figure 5.12).

Weight change behavior of NITE SiC samples due to thermal cycling in hot hydrogen is exhibited in figure 5.13. For temperatures of both 2000 and 2250 K, similar to the intrinsic compatibility of SiC with hydrogen probed with CVD SiC, no weight gain occurs, however, NITE SiC exhibits sublinear mass loss kinetics. This trend does not indicate that the sintering additives in NITE SiC exhibit a passivating surface microstructure when exposed to very high temperature hydrogen environments. Instead, the presence of sintering additives enhance SiC corrosion. As shown in figure 5.14., when comparing the weight change behavior of NITE SiC with CVD SiC for the same exposure conditions, NITE SiC exhibits an order of magnitude total mass loss higher ($0.65 \pm 0.03 \text{ mg/mm}^2$, 2000 K) than that of CVD SiC ($0.052 \pm 0.003 \text{ mg/mm}^2$, 2000 K) for low temperature exposures. At high temperatures, NITE SiC exhibits an order of two higher magnitude mass loss ($1.11 \pm 0.05 \text{ mg/mm}^2$, 2250 K and $1.97 \pm 0.10 \text{ mg/mm}^2$, 2500 K) than CVD SiC ($0.42 \pm 0.02 \text{ mg/mm}^2$, 2250 K and $0.94 \pm 0.05 \text{ mg/mm}^2$, 2473 K).

Figure 5.15 corresponds to typical surface microstructures of NITE SiC exposed to flowing hydrogen for 120 minutes at a temperature of 2000 K. After exposure to 2000 K, the exposed microstructure is extremely porous and defected. Unlike typical microstructures of CVD SiC, no large regions of Si condensate are present on the surface. Instead, the NITE SiC surface region shows evidence of extensive intergranular attack and corrosion pitting, with pit diameters exceeding 100 microns in the most severe areas. Regions with the least corrosion pitting exhibit microstructural segregation, which is most likely due to segregation and preferential diffusion of the oxide additives out of the surface microstructure. Microstructural segregation appears to precede the formation of corrosion pits. Fully formed corrosion pits are depleted in the segregated secondary phase. Corrosion pits in the process of formation are rich in the secondary phase that appears to act as a pathway for localized hydrogen attack. Yttria (Y_2O_3) and alumina (Al_2O_3) sintering additives may interact with hydrogen to either reduce to form free metal or volatile oxides.



Figure 5.12 NITE SiC exposure at 2500 K resulted in significant enough corrosion to completely obscure the top viewport of the CFEET furnace.

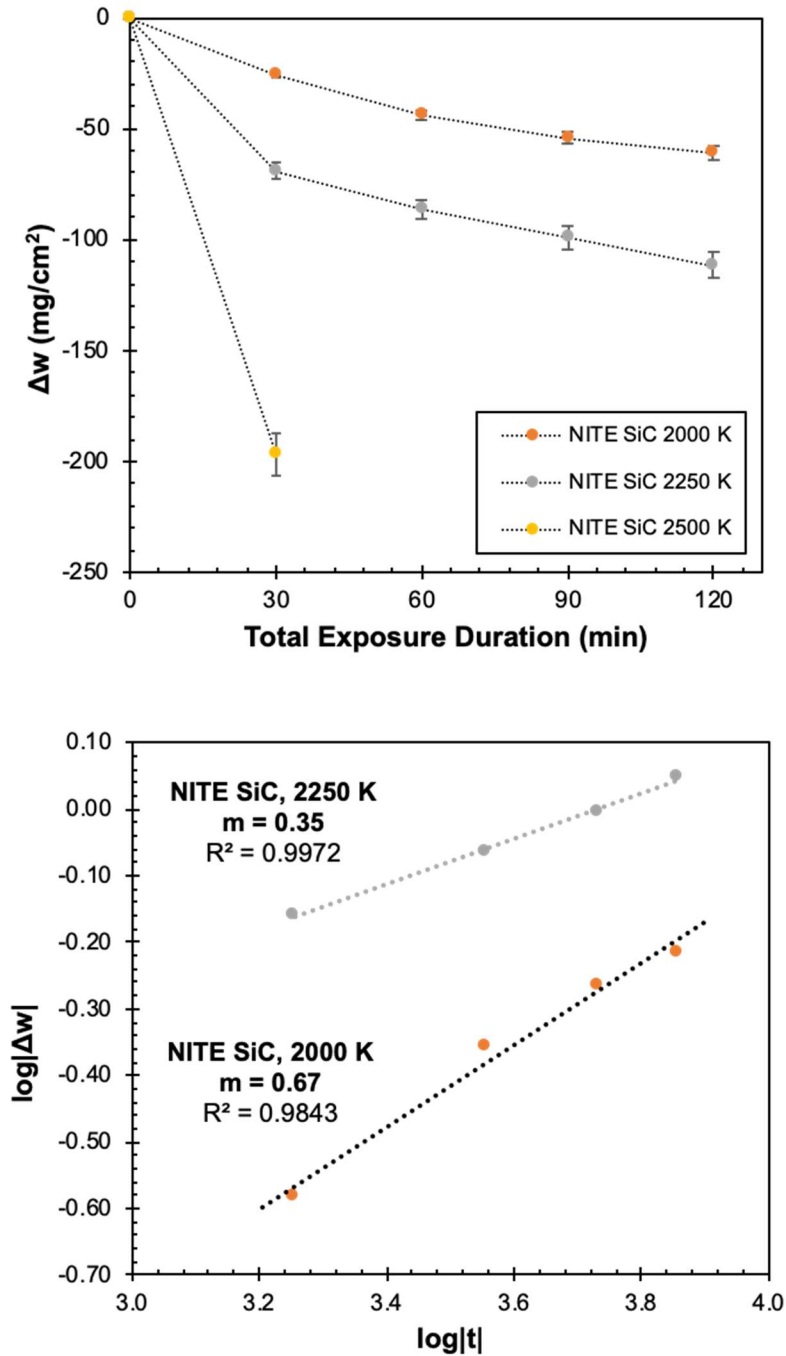


Figure 5.13 (a) NITE SiC weight change behavior observed from thermal cycling experiments in flowing hydrogen at temperatures between 2000 – 2500 K. Only one thermal cycle was completed at 2500 K. (b) At temperatures of 2000 K and 2250K, NITE SiC exhibits sublinear weight change behavior.

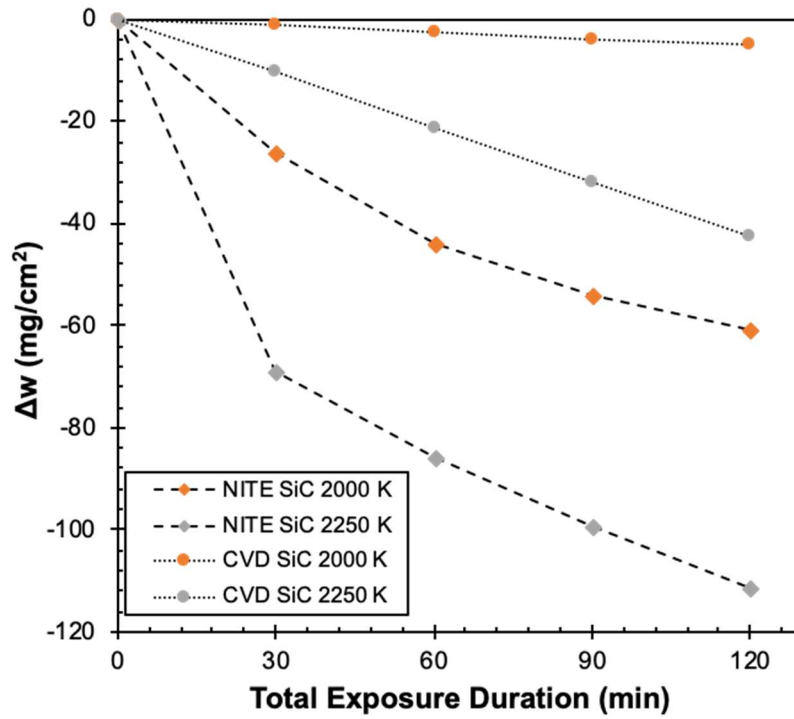
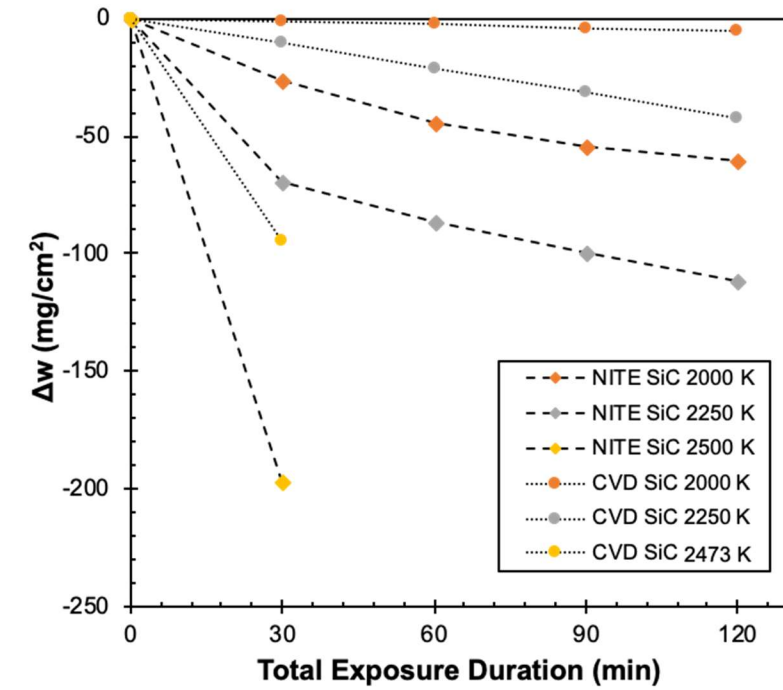


Figure 5.14 Comparison of NITE SiC and CVD SiC weight change behavior under hot hydrogen thermal cycling conditions.

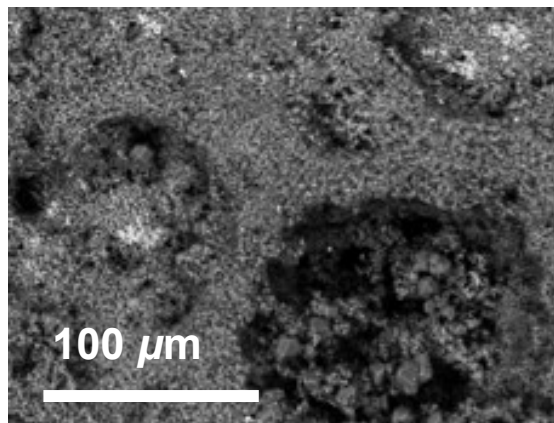
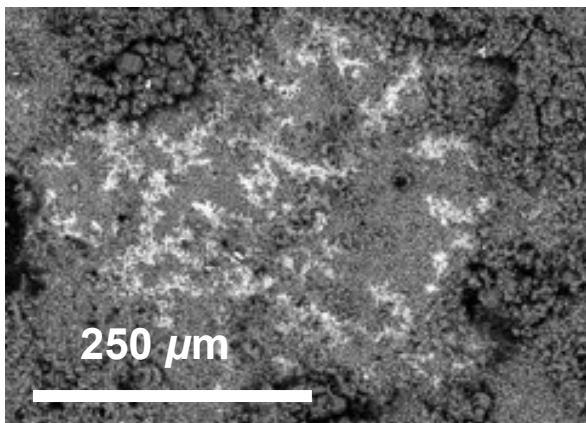
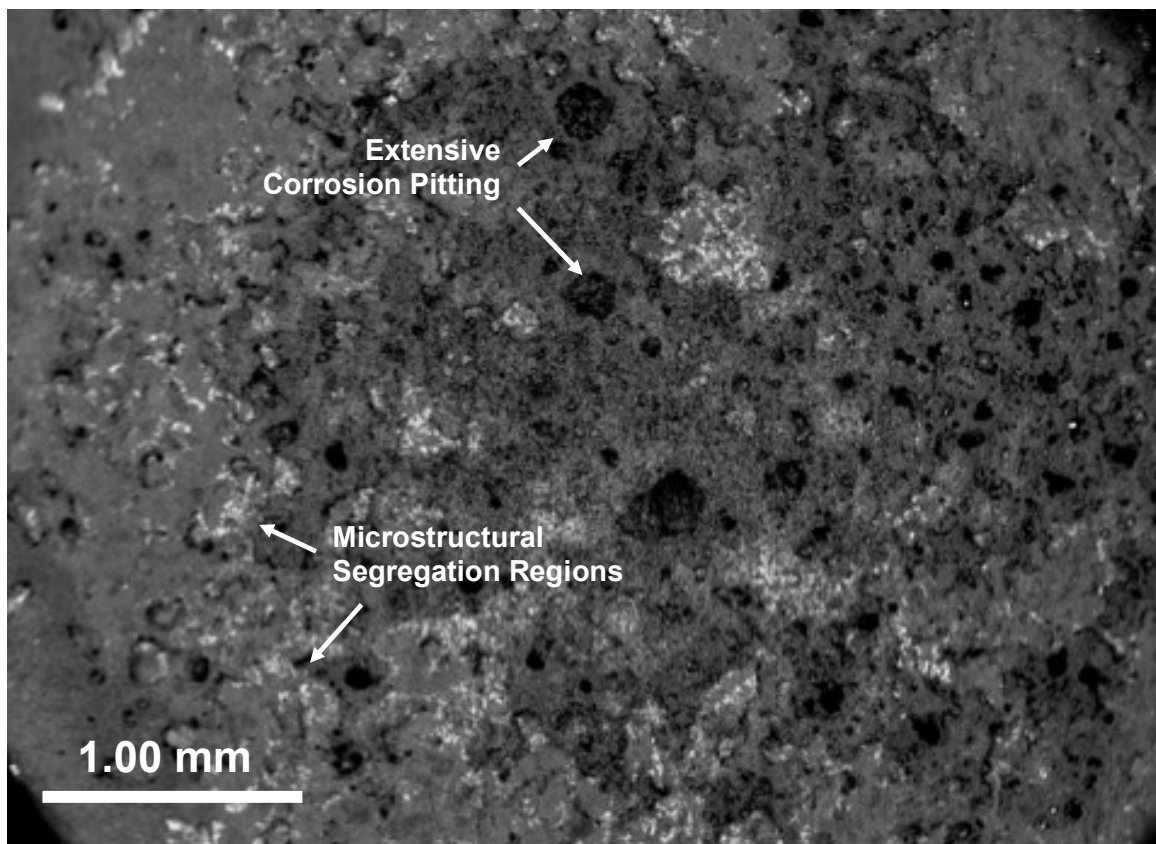


Figure 5.15 Backscatter electron images of NITE SiC surface microstructure exposed to 2000 K, flowing hydrogen.

This phenomenon suggests localized corrosion of the NITE SiC is initiated by the compositional segregation of the NITE SiC surface microstructure, preferential migration of sintering aids to diffuse out of the matrix may provide a pathway for H₂ diffusion into the matrix to enhance weight loss. Figure 5.16 shows results from EDS Mapping of NITE SiC cross sections exposed to flowing hydrogen for 120 minutes at 2000 K. The outer radial microstructure exhibits segregation of C, O, Si, Y, and Al after exposure. Preferential segregation of O and C towards the surface region is present and the near surface region is poor in Al and Y, indicating preferential corrosion of additive oxides during hydrogen exposure. However, the bulk microstructural (midsection) region is relatively unperturbed. Removal of the oxide rich regions (originally located at the grain boundaries) can leave the surface microstructure porous and vulnerable to localized corrosive attack of SiC grains, which is evidenced by extensive corrosion pitting and porosity of the surface microstructure.

Corrosion pits enhance hydrogen ingress into the matrix (localized corrosion), increasing the surface area available for corrosive interaction and preferential removal of sintering additives. This results in observed mass losses significantly higher than that of high purity SiC interactions. However, as the oxide rich phase is removed from the surface, corrosion rate decreases as hydrogen penetration and corrosion product removal from deeper into the microstructure is required, resulting in sublinear weight change behavior. Evidence of free, delineated grains of SiC at the surface and within corrosion pits suggest that volatilization of exposed SiC grains by grain boundary attack plays a primary role in NITE SiC corrosion at low exposure temperature.

At temperatures of 2250 K and greater, the oxide rich eutectic is no longer prevalent on the surface of NITE SiC (figure 5.17). Instead, for these exposure conditions, two regions are observed along the sample surface, an outer radial region (corresponding to parallel to the flow direction) exhibits a disordered structure and an inner region (corresponding to normal to the flow direction) exhibits extensive grain boundary attack and intergranular corrosion of SiC grains. In the normal flow region, large (10 – 50 μm) exposed SiC grains much larger than that of the parent material may suggest grain growth occurs with high temperature exposure due to the loss of the oxide eutectic at the grain boundaries. Small Y-rich condensate is visible on the surface of the NITE SiC microstructure (figure 5.18). EDS mapping of NITE SiC exposed to 2250 K shows similar trends to the corrosion behavior observed at 2000 K. Similar to 2000 K exposures, the outer radial region ($\sim 250 - 500 \mu\text{m}$), is depleted in the oxide additives. However, porosity is no longer constrained to the outer radial region (figure 5.19). Large (100 – 1000 μm depth) localized corrosion pipe regions are formed. When comparing the corrosion kinetics of NITE SiC exposed

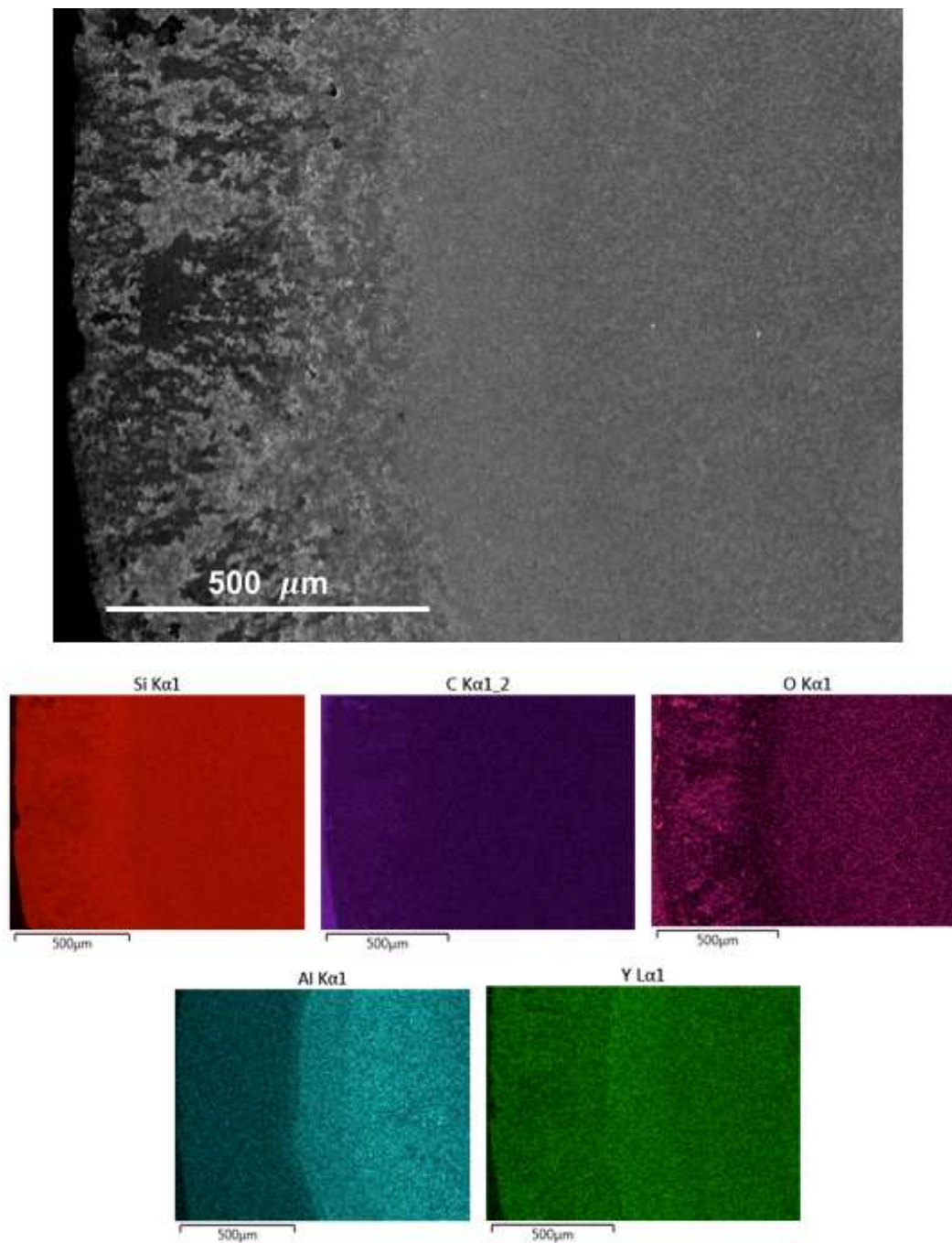


Figure 5.16 Backscatter electron micrograph of NITE SiC outer radial microstructure after exposure to flowing hydrogen at 2000 K for 120 minutes.

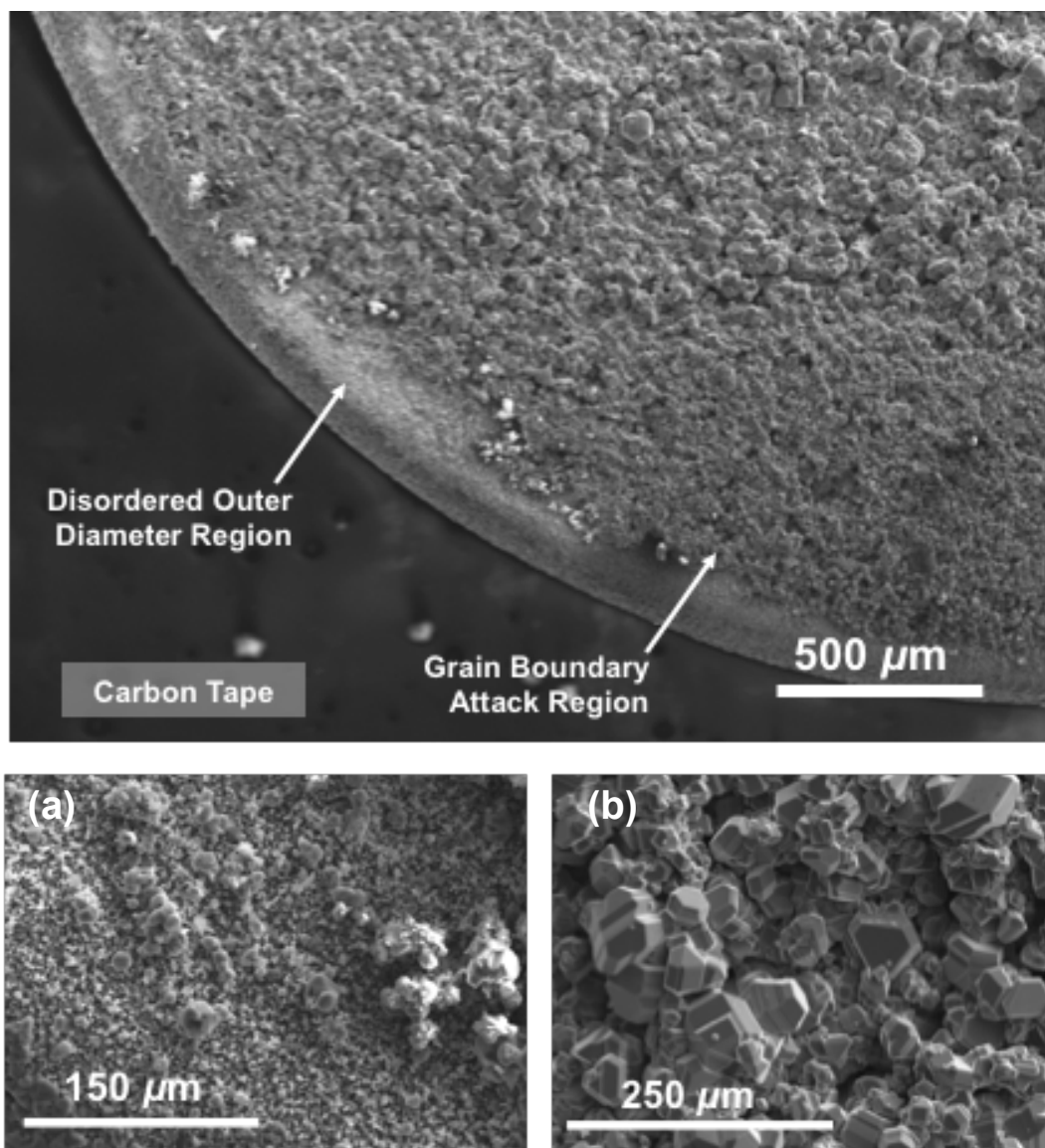


Figure 5.17 Scanning electron micrographs of the surface microstructure of NITE SiC exposed to flowing hydrogen at 2250 K. In the outer diameter region, where flow is parallel to the surface, the structure is highly disordered with an Si rich signature (a). In the inner region, corresponding to normal flow of hydrogen, no presence of free Si or sintering additives is observed (b). Extensive grain boundary attack and intergranular attack is evident in this region.

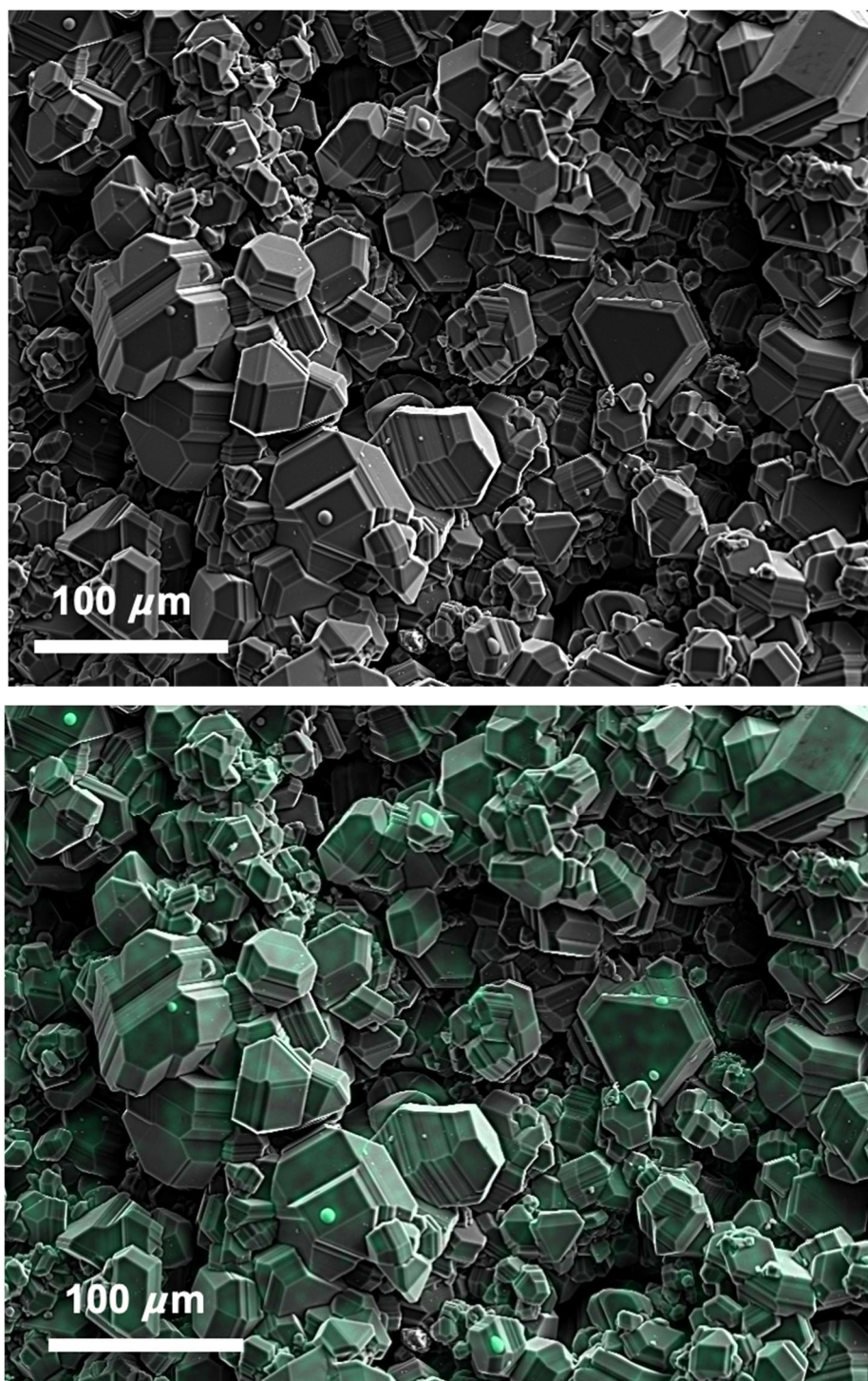


Figure 5.18 Typical surface microstructure of NITE SiC exposed to 2250 K in the normal flow region, showing the formation of condensed corrosion products on the surface (top). Map of Y-L α counts for EDS mapping (bottom).

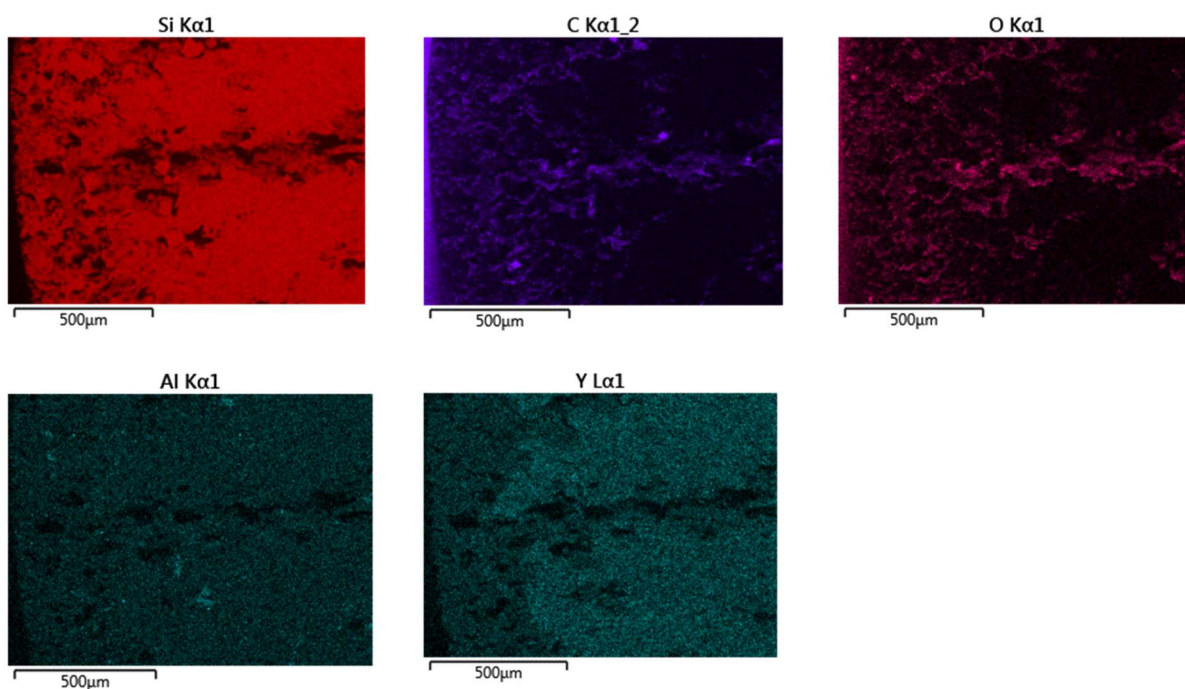
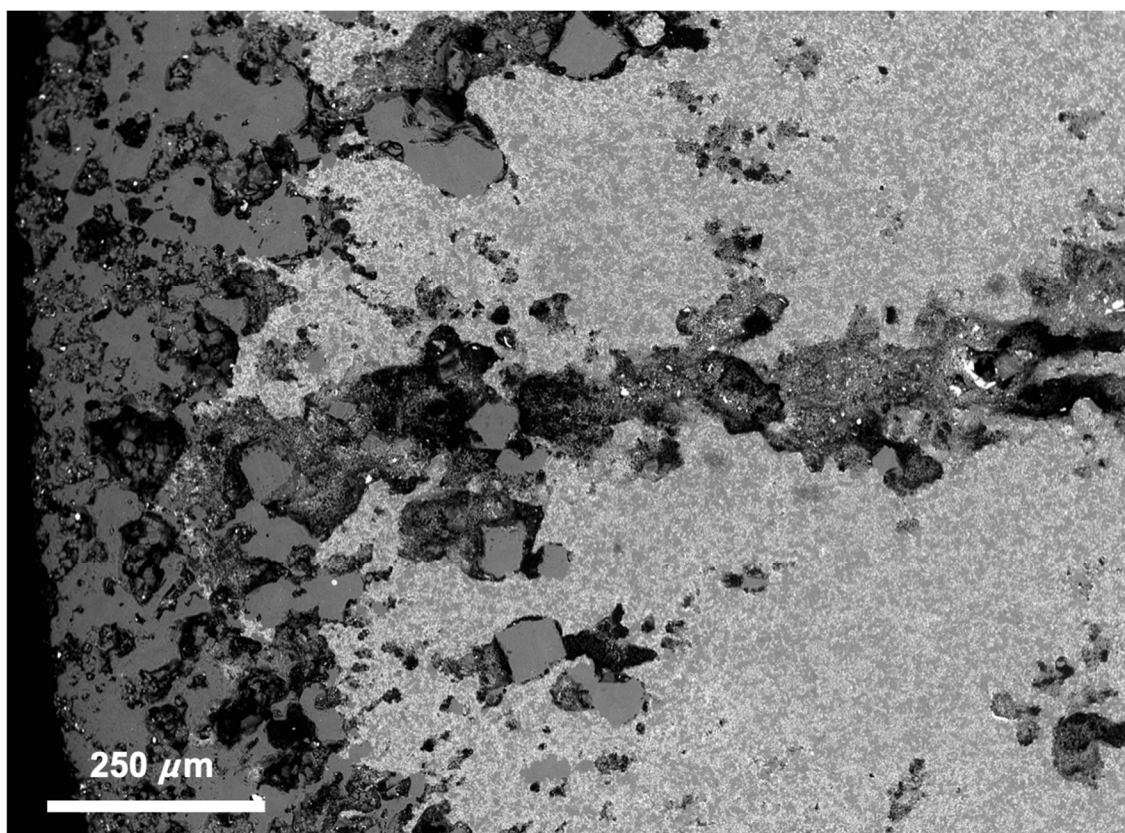


Figure 5.19 Cross sectional view of NITE SiC microstructure exposed to hydrogen at 2250 K for 120 minutes.

to 2000 K and 2250 K, corrosive mass loss exhibits a much greater temperature dependence for higher temperature exposures. This may be due to the high initial mass loss rate observed for 2250 K exposure. Higher corrosion rates and diffusivities at higher exposure temperature allow for more rapid segregation, diffusion, and removal of the oxide sintering additives, resulting in a non-linear approach to a steady state corrosion rate at higher temperatures (figure 5.20).

Comparison of NITE SiC and CVD SiC Corrosion Kinetics

Average mass loss rates of high temperature thermal cycling were compiled with results from low temperature duration testing of NITE SiC. Results from both test series are shown in figure 5.21. Observed mass loss rates of NITE SiC following both thermal cycling and long hold duration testing (1173 – 2500 K) exhibit an Arrhenius temperature dependence. Two regimes are apparent for NITE SiC, a passive low temperature regime and a high temperature regime with a high activation energy with a transition at approximately 1573 K (1300 °C). The transition temperature between the two regimes corresponds roughly to the temperature at which free Si is no longer stable as a solid corrosion product on the sample surface. At this point, observed corrosion rates rapidly increase with a derived apparent activation energy of 290 +/- 14 kJ/mol.

NITE SiC exhibits significantly greater degradation than CVD SiC for all exposure times and temperatures with a lower apparent activation energy (figure 5.22). SEM and EDS microstructural analyses of NITE SiC cross sections showed the near surface region (~ 500 μm) to be depleted in Y and Al rich additives at 2000 K. Therefore, the preferential volatilization of oxide rich additives Y_2O_3 and Al_2O_3 were attributed to the initial rapid weight loss of NITE SiC. The preferential volatilization of sintering additives results in a lower apparent activation energy of NITE SiC (290 +/- 14 kJ/mol) compared to CVD SiC (370 +/- 19 kJ/mol). Therefore, due to competing effects of preferential sintering additive volatilization, thermodynamic instability, and matrix corrosion, the boundary layer diffusion limited gas transport model was not acceptable for use or adaptation to model NITE SiC corrosion in a hydrogen environment (figure 5.23).

Microstructural Stability NITE SiC for Exposure Temperatures of 2000 – 2500 K

Figure 5.24 exhibits backscatter electron images of the bulk microstructure of NITE SiC after 120 minutes exposure at 2000 and 2250 K, as well as 30 minutes exposure at 2500 K. At 2000 K, the bulk microstructure is compositionally stable, and porosity is confined to the outer radial region. Unlike the stable bulk microstructural region exhibited by NITE SiC at 2000 K, at temperature exposures greater than the typical NITE SiC hot press temperatures, bulk NITE SiC

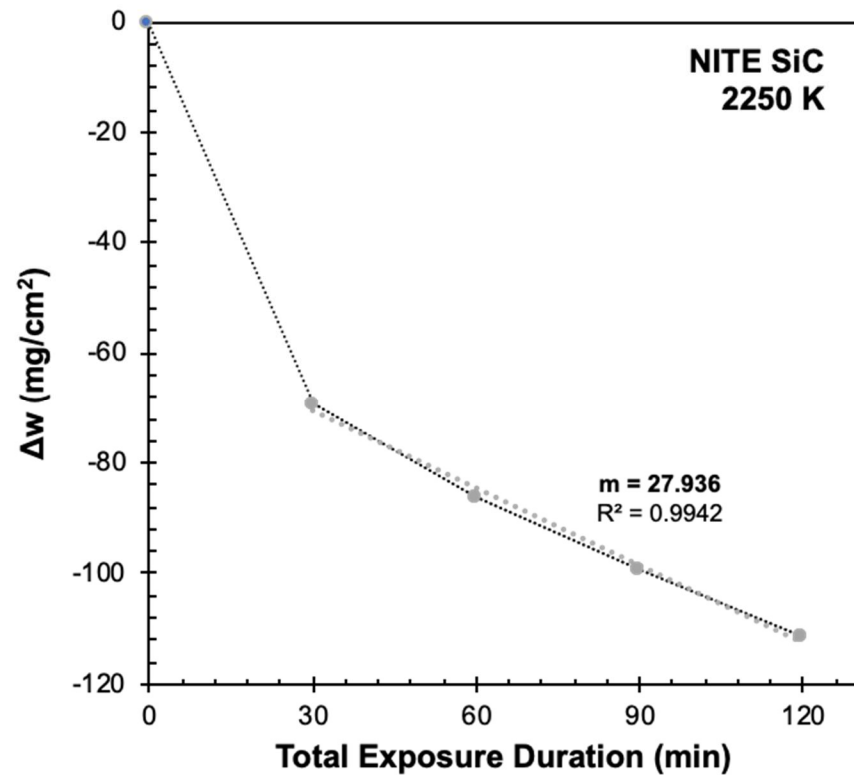


Figure 5.20 Mass loss of NITE SiC during thermal cycling exposure exhibits an initial transient of high mass loss followed by a trend towards linear mass loss rates.

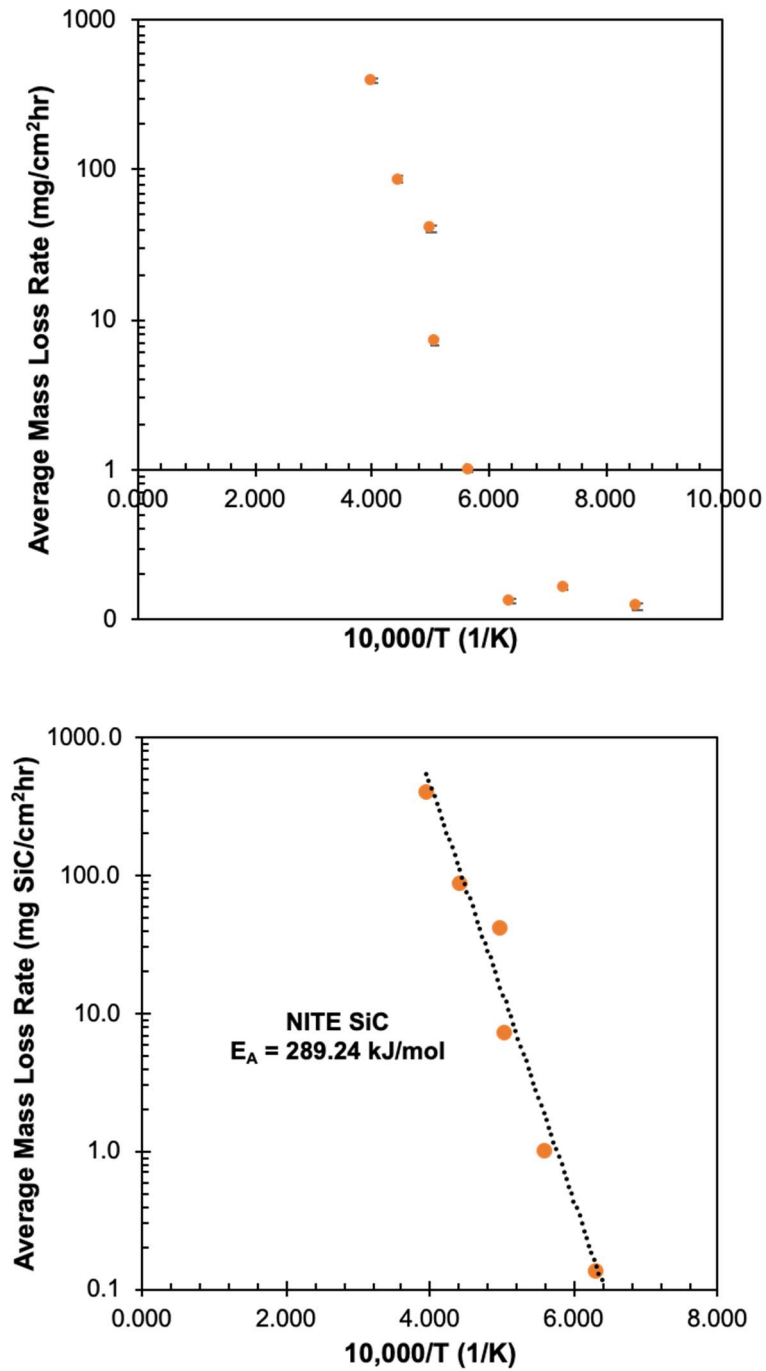


Figure 5.21 Temperature dependence of average mass loss rates observed of NITE SiC in flowing hydrogen for various temperatures.

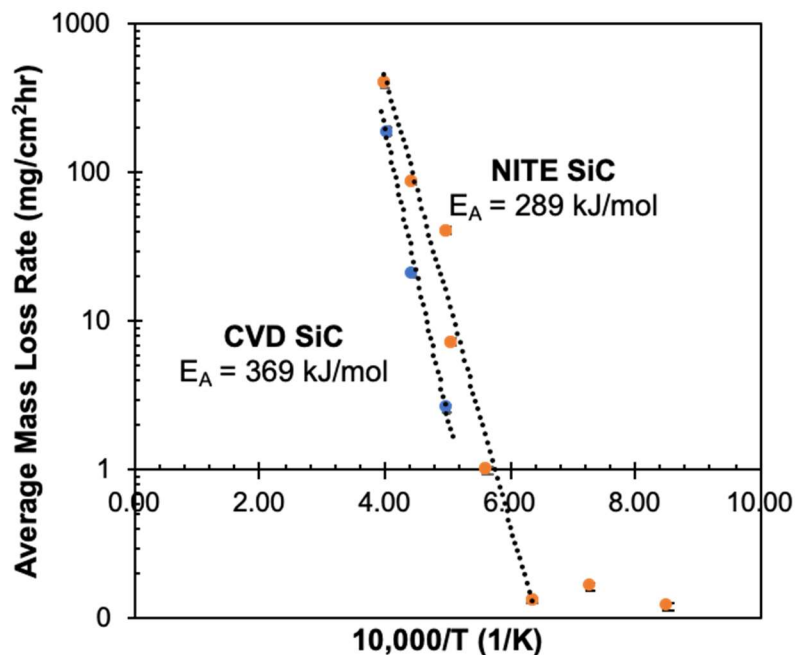


Figure 5.22 Comparison of the Arrhenius behavior of CVD and NITE SiC in hot hydrogen evaluated with average mass loss rates calculated from weight change behavior over total time.

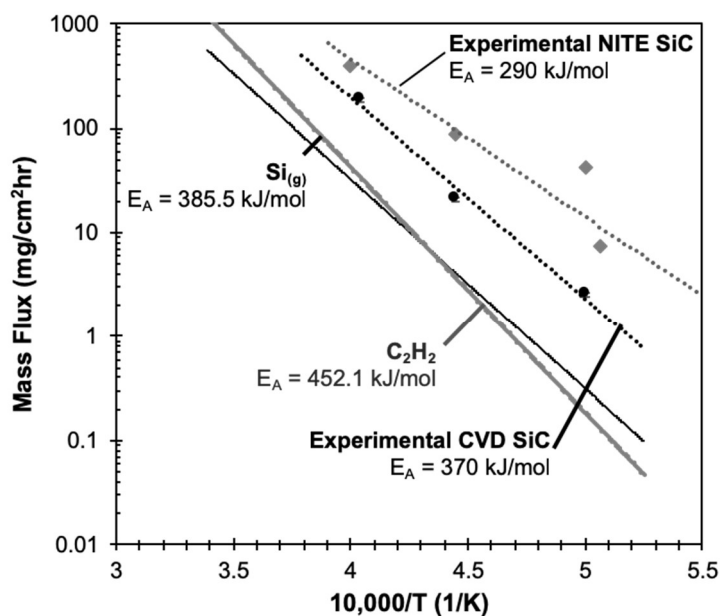


Figure 5.23 Comparison of the temperature dependence of experimentally observed NITE and predicted mass loss rates of SiC using the boundary layer diffusion gas transport model.

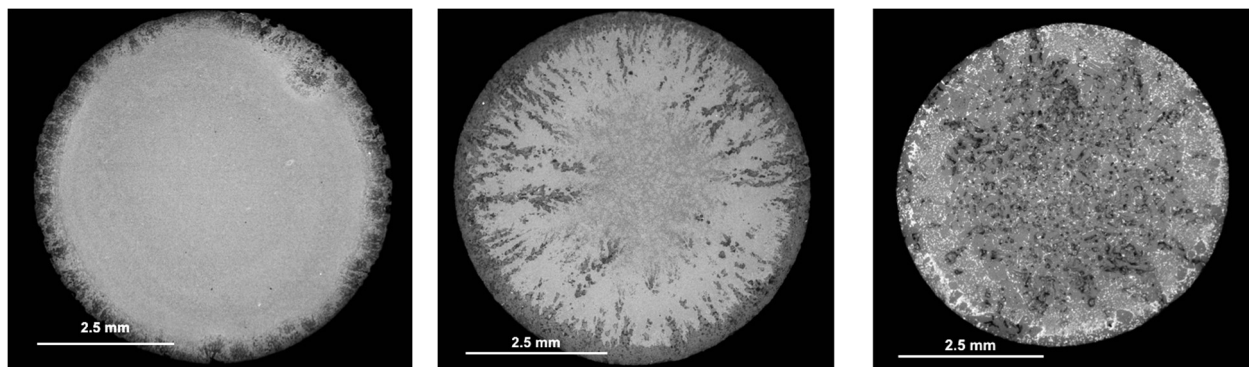


Figure 5.24 Comparison of internal microstructures of NITE SiC after exposure to flowing hydrogen (a) 2000 K, 120 minutes (b) 2250 K, 120 minutes (c) 2500 K, 30 minutes.

microstructure evolves. At 2250 K, while porosity is constrained to the outer radial region, the oxide-rich eutectic, which is predicted to be liquid phase for high temperature exposures, begins to agglomerate and segregate rather than exist uniformly throughout the bulk microstructure (figure 5.25). Bulk migration of the eutectic towards the surface region is observed. At 2500 K exposures, the eutectic composition is no longer stable in NITE SiC with the transition metal rich secondary phases preferentially migrate towards the surface region. Following hot hydrogen exposure, bulk compositional segregation occurs with the formation of Y rich secondary phases that attract Zr impurities (figure 5.26). The microstructure degrades to form a highly porous structure with interconnected porosity. This may be indicative that the gas stream fully diffused through the microstructure for a bulk combustion of the sample during testing at these conditions.

Powder XRD measurements were performed on NITE SiC and CVD SiC samples exposed to 2000 – 2500 K to compare the compositional stability of NITE SiC to CVD SiC. XRD measurements undertaken after hot hydrogen exposure of CVD SiC shows overall compositional stability of SiC after exposure to hot hydrogen in both the near surface microstructure (Figure 5.27). New peaks at 2θ values of 34, 37.5° occur at exposure temperatures exceeding 2250 K. Peaks at these positions may be caused either presence of stacking faults or change in phase from a cubic to hexagonal polymorph, such as 6H SiC (α -SiC). Compared to cubic SiC polymorphs, hexagonal SiC may be expected to exhibit higher thermodynamic stability at temperatures greater than ~2200 K at 1 atm over pressure [95], however thermodynamic calculations did not predict a phase transition for the hydrogen environment.

Powder XRD scans of the NITE SiC surface microstructure demonstrate that following H₂ exposure at temperatures greater than 2000 K, the formation of new peaks at low 2θ values are present in the near surface microstructure of exposed NITE SiC samples (figure 5.28). At 2250 K, new peaks between 2θ values of 20 – 30° are attributed to formation of a Si rich microstructure and evolution in the eutectic structure after exposure to long durations (120 minutes) at temperatures exceeding the eutectic temperature of NITE sintering additives and the SiC matrix.

At 2500 K, a high frequency of low intensity peaks are present between 2θ values of 30 – 35°. The formation of these peaks indicates either formation of secondary phases present at low concentrations or formation of an alternative secondary phase with a large disordered structure. Probable phases, which may be stable at 2500 K, may be either free metal (Y), or transition metal silicides or carbides (such as YC₂). A new high intensity peak at 38° indicates the formation of a secondary SiC polytype 4H-SiC following 2500 K exposure.

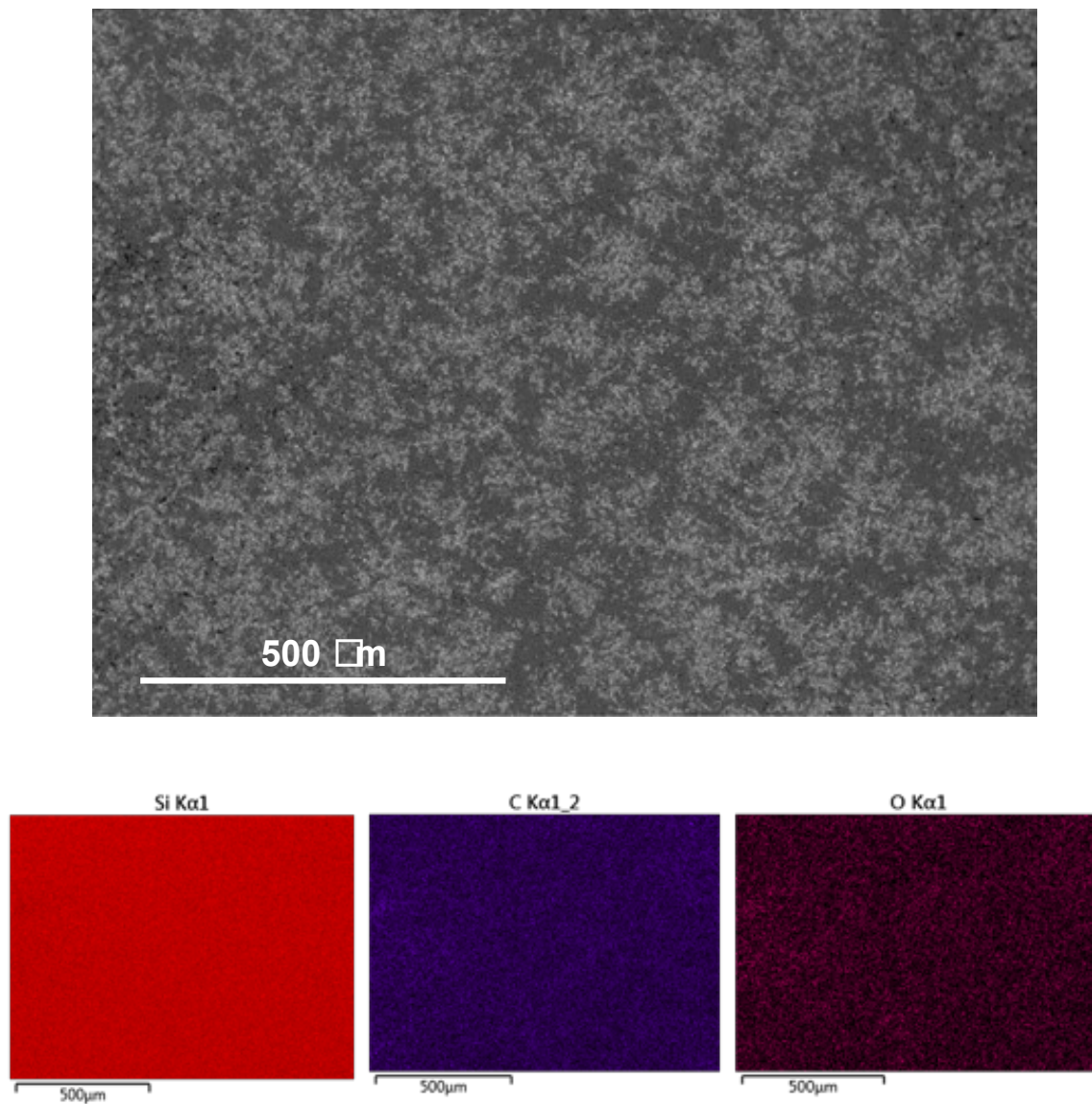


Figure 5.25 Backscatter electron micrograph of NITE SiC bulk microstructure after exposure to flowing hydrogen at 2250 K for 120 minutes.

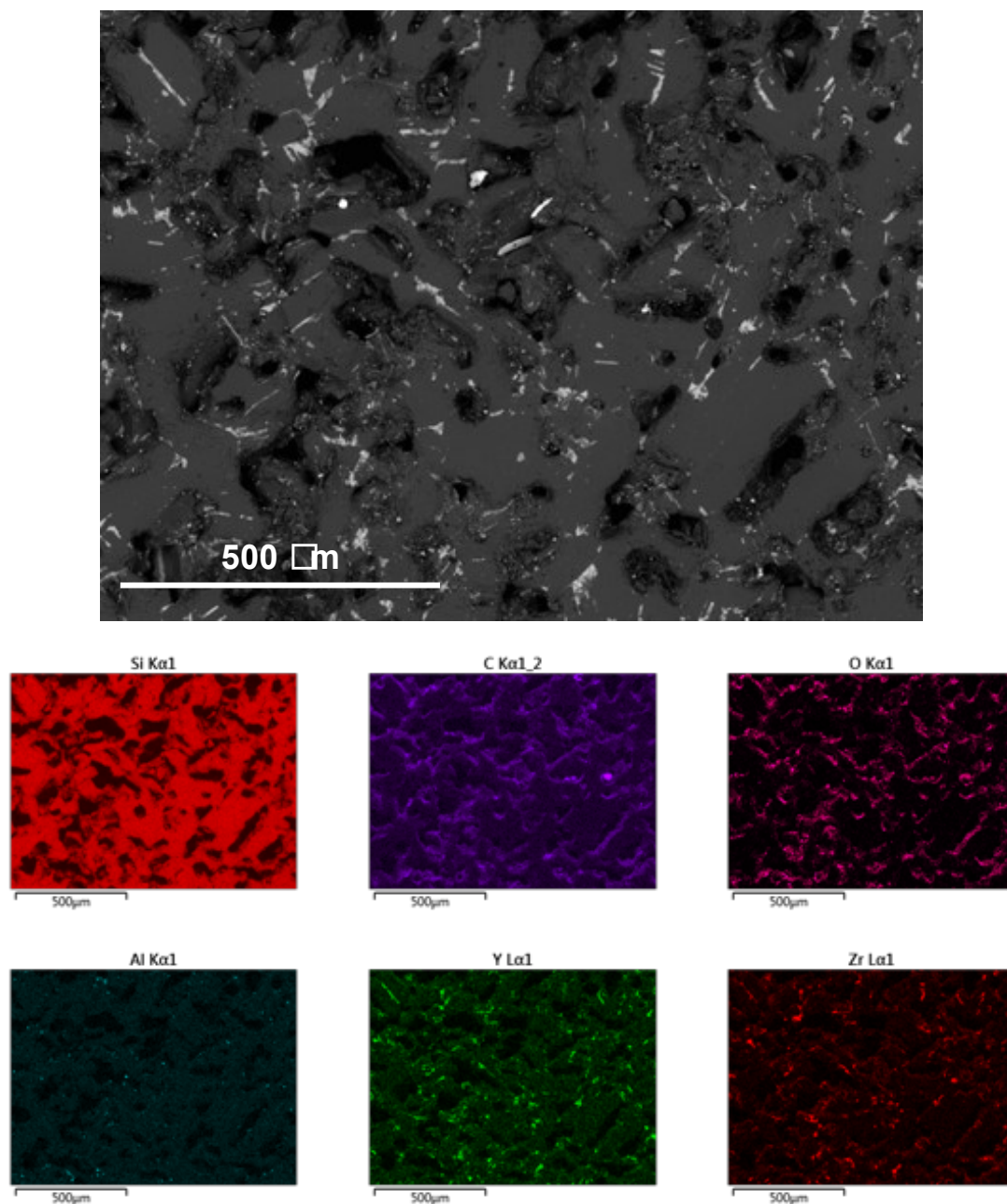


Figure 5.26 Backscatter electron micrograph of NITE SiC bulk microstructure after exposure to flowing hydrogen at 2500 K for 30 minutes.

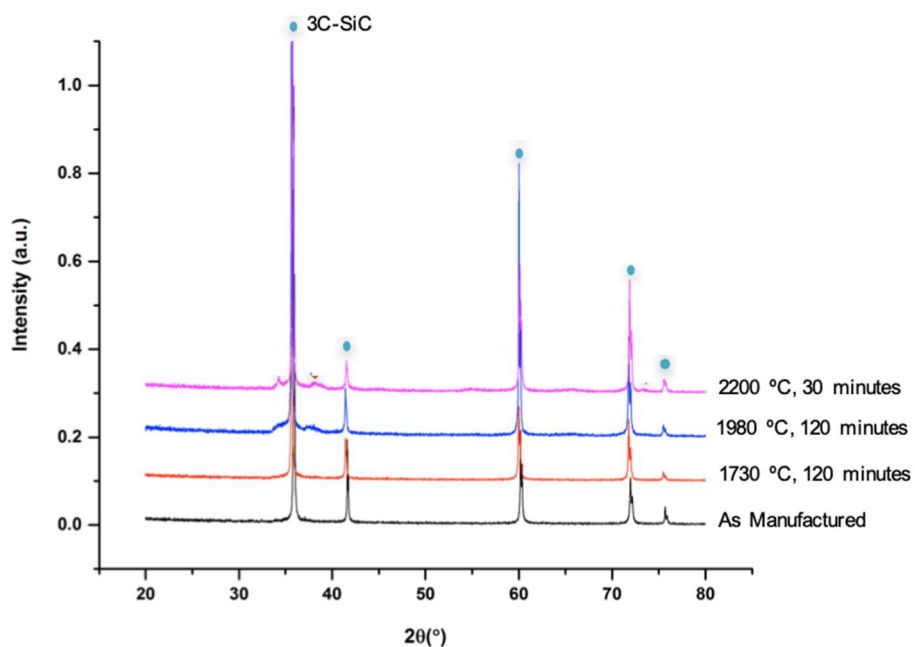


Figure 5.27 Representative XRD spectra of the near surface microstructure of CVD SiC exposed to flowing hydrogen at temperatures of 2000, 2250, and 2473 K.

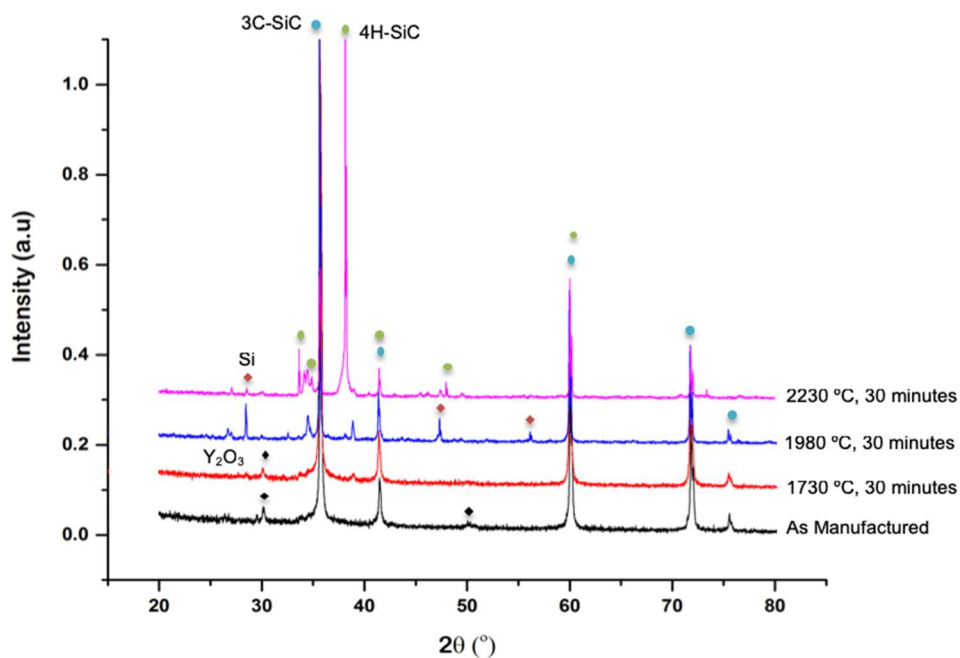


Figure 5.28 XRD spectra of near surface microstructures of NITE SiC exposed to flowing hydrogen at temperatures between 2000 – 2500 K.

Discussion of Results

Due to competing effects of preferential sintering additive volatilization, thermodynamic instability, and matrix corrosion, the boundary layer diffusion limited gas transport model was not acceptable for use or adaptation to model NITE SiC corrosion in a hydrogen environment. Average mass loss rates of NITE SiC were evaluated to be greater than historically derived limits ($\sim 16.2 \text{ mg/cm}^2\text{hr}$) for NTP engines for temperatures exceeding 1773 K, therefore use of an uncoated NITE SiC matrix FCM type fuel is not competitive for high performance NTP applications compared to historic coated graphite composite type fuels. Reduction of additive sintering oxides and use of high purity SiC or other chemically compatible coatings may enable higher operating temperatures by preventing the preferential loss of sintering additives and corrosion pitting behavior exhibited by NITE SiC. However, use of NITE SiC as a structural fuel matrix should be limited to $\sim 2250 \text{ K}$. At temperatures exceeding 2250 K, bulk reaction and segregation of the oxide eutectic with the matrix material results in significant degradation of the bulk matrix at timescales (30 minutes) much less than that typically proposed for NTP engine lifetimes (45 – 109 minutes).

NITE SiC corrosion behavior was assessed in hot hydrogen for the temperature regime between 1173 – 2500 K. Similar to CVD SiC, NITE SiC was unstable in hot hydrogen and exhibited negative weight change behavior in hot hydrogen via volatilization reaction. However, examination of NITE SiC corrosion kinetics through thermal cycling experiments showed a sublinear dependence of NITE SiC weight change with exposure duration and degradation of NITE SiC in hydrogen was significantly enhanced compared to CVD SiC. SEM and EDS microstructural analyses of NITE SiC cross sections showed the near surface region ($\sim 500 \text{ }\mu\text{m}$) to be depleted in Y and Al rich additives at 2000 K. Therefore, higher mass losses and sublinear behavior is attributed to preferential loss of sintering additives from the surface for temperatures of 2000 K or less. Preferential mass losses of sintering additives also attributed to lower apparent activation energies of NITE SiC in hot hydrogen ($\sim 290 \text{ kJ/mol}$) compared to CVD SiC ($\sim 370 \text{ kJ/mol}$). The activation energy for NITE SiC was comparable to experimentally derived activation energies of alternative sintered SiC materials such as SASC ($\sim 270 \text{ kJ/mol}$) [72]. Due to the lower required activation energy of NITE SiC compared to intrinsic SiC values, typical mass loss rates were much higher for NITE SiC than CVD SiC, i.e. $2.585 \text{ mg/cm}^2\text{hr}$ versus $40.72 \text{ mg/cm}^2\text{hr}$ respectively at 2000 K.

The bulk microstructure of NITE SiC is stable at 2000 K, although uncoated samples should anticipate near surface region to become depleted in Y_2O_3 and Al_2O_3 additives, resulting in extensive corrosion pitting. At 2250 K and 2500 K, oxide additives interact with the bulk microstructure forming large pockets of impurity-rich secondary phases. The intrinsic stability of NITE SiC in hot hydrogen is only acceptable up to ~2250 K due to evolution of the microstructure to form secondary phases and protective coatings should be utilized in order to achieve acceptable mass loss behavior at intermediated temperatures (1773 – 2250 K). Use of FCM derivative NITE SiC matrix fuels for NTP applications is limited to low performing NTP systems, assuming maximum H_2 outlet temperatures of ~2000 K, results in anticipated I_{sp} values of ~750 s. This is still a significant increase (> 50%) compared to best performing chemical engines (450 s) and may also present a higher development, near term alternative to recapturing fabrication processes of LEU derivative historic NTP fuel forms. Alternative uses of NITE SiC FCM fuels include the reactor “cold end” and “mid band” regions to provide higher fuel loadings and more desirable corrosion behavior. Nevertheless, development of fuel systems capable of withstanding higher operating temperatures is still required for the “hot end” of high performing NTP systems.

Due to excessive corrosion related to the oxide additives and their incompatibility with SiC in a hydrogen environment at very high temperatures, the use of NITE SiC in the operating temperature regime of typically proposed NTP systems ($T > 2250$ K) requires identification of alternative sintering additives that are compatible with the SiC matrix at temperatures in excess of 2250 K or the development of highly robust surface coatings. Further development may look at extension of the NITE fabrication process to alternative matrix candidates such as TiC and ZrC, which requires identification of appropriate sintering additives and fabrication parameters which also allow for compatibility with the TRISO fuel particle design.

Intrinsic Stability of TMCs in Hydrogen

Observed Corrosion Kinetics of TiC and ZrC in Flowing Hydrogen

Mass loss of titanium carbide observed during thermal cycling at 2000 and 2250 K is presented in figure 5.29. Titanium carbide exhibits sublinear mass loss for each condition. At 2000 K, mass loss behavior best fits a $\frac{1}{2}$ power parabolic trend, maximum mass loss observed was less than 2.0 mg/cm², slightly less than that seen for CVD SiC. With increasing temperature, the trend becomes increasingly sublinear. There was no trend in mass loss with increasing flow velocity, suggesting that the corrosion reaction is not mass transfer dependent like SiC (surface reaction limited) (figure 5.30).

Microstructural evaluation was undertaken to investigate the microstructural response to hydrogen corrosion at elevated temperatures. The bulk microstructural stability was accessed using XRD (figure 5.31). There was no evidence of formation of secondary peaks in TiC XRD Spectra. Overall, investigation of the bulk microstructure indicated peak sharpening was observed and there was a shift in peak values to higher 2θ values, which indicated sintering during high temperature exposure. In the near surface microstructure, shifts in peak positions to higher 2θ , was also observed, however asymmetric peak broadening to higher 2θ values were observed for both temperatures (figure 5.32). Asymmetric broadening of peaks indicates a highly defected/strained microstructure after exposure to hydrogen.

Analysis of the near surface microstructure using SEM showed two dominant microstructural regions of TiC after exposure to hydrogen thermal cycling at 2000 K (figure 5.33). In the central regions of sample pins grain boundary attack of as sintered TiC grains is the primary mode of degradation to the sample surface. The outer radial region (corresponding to parallel flow) exhibited extensive corrosion pitting of exposed grains and formation of a carbon rich precipitates in the grain boundaries which form a continuous web-like structure. At temperatures exceeding 2250 K, seeding secondary boron rich phases can be identified. The boron rich phase was not present in significant enough concentrations to be identified by XRD. Pick up of boron as an impurity in the hydrogen gas stream may lead to suppression of the apparent corrosion rate and attribute to increasing sub linearity with increased temperature.

Mass loss of ZrC as a result of flowing hydrogen exposure at temperatures of 2000, 2250 K is shown in figure 6.9. Similar to TiC, ZrC exhibits sublinear weight change behavior for each thermal cycle (figure 5.34). Mass loss in flowing hydrogen was observed to higher when exposed to

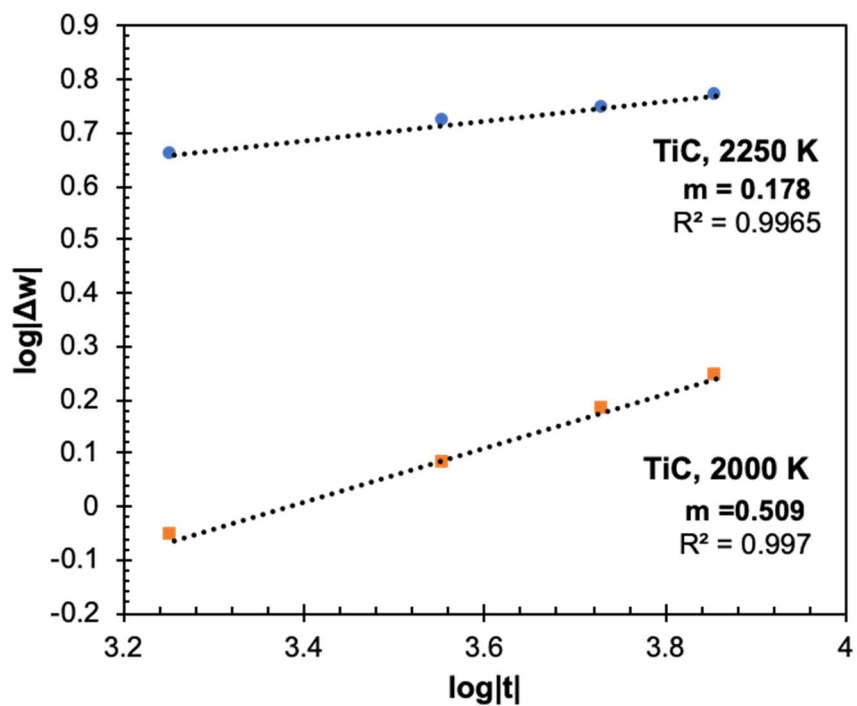
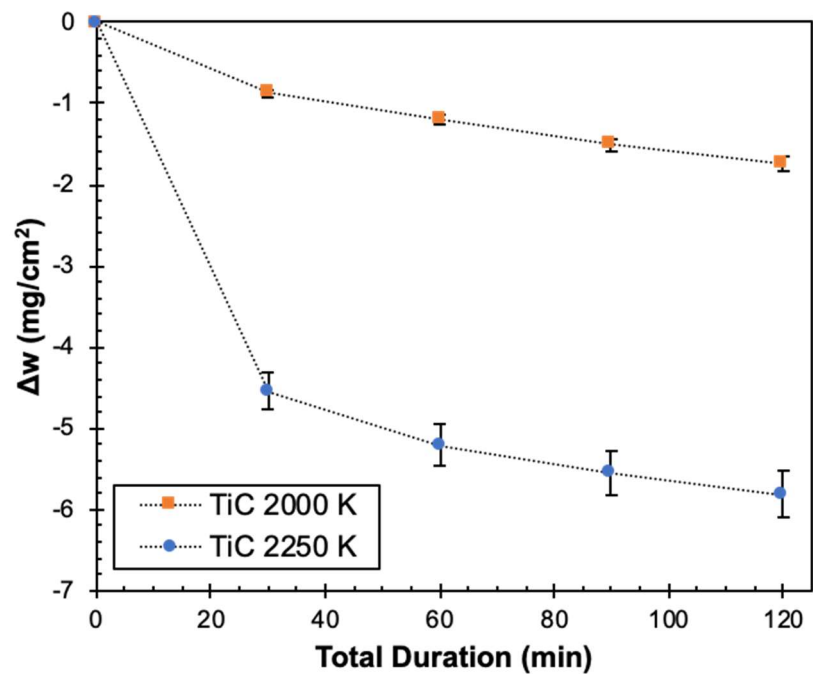


Figure 5.29 Weight change behavior of sintered TiC after exposure to flowing hydrogen at 2000, 2250 K for 120 minutes. TiC exhibits nonlinear weight loss in flowing hydrogen, which increases with increasing temperature.

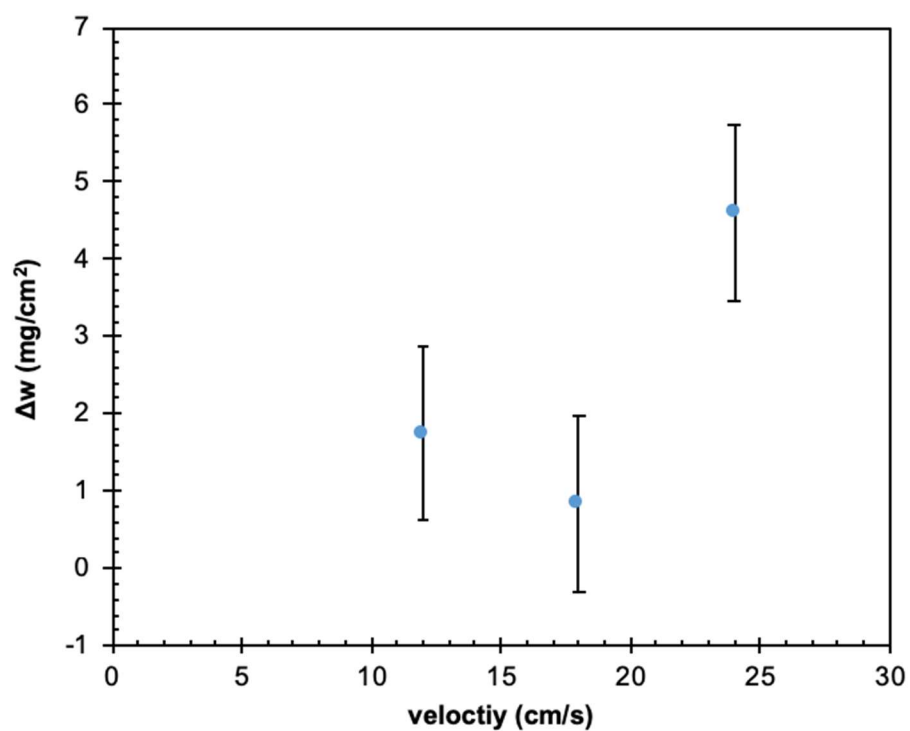


Figure 5.30 Weight change behavior of sintered TiC after exposure to flowing hydrogen at 2000 K, 30 minutes for gas flow velocities of 12.06, 18.09 24.12 cm/s. TiC weight change did not exhibit a dependence on gas stream velocity.

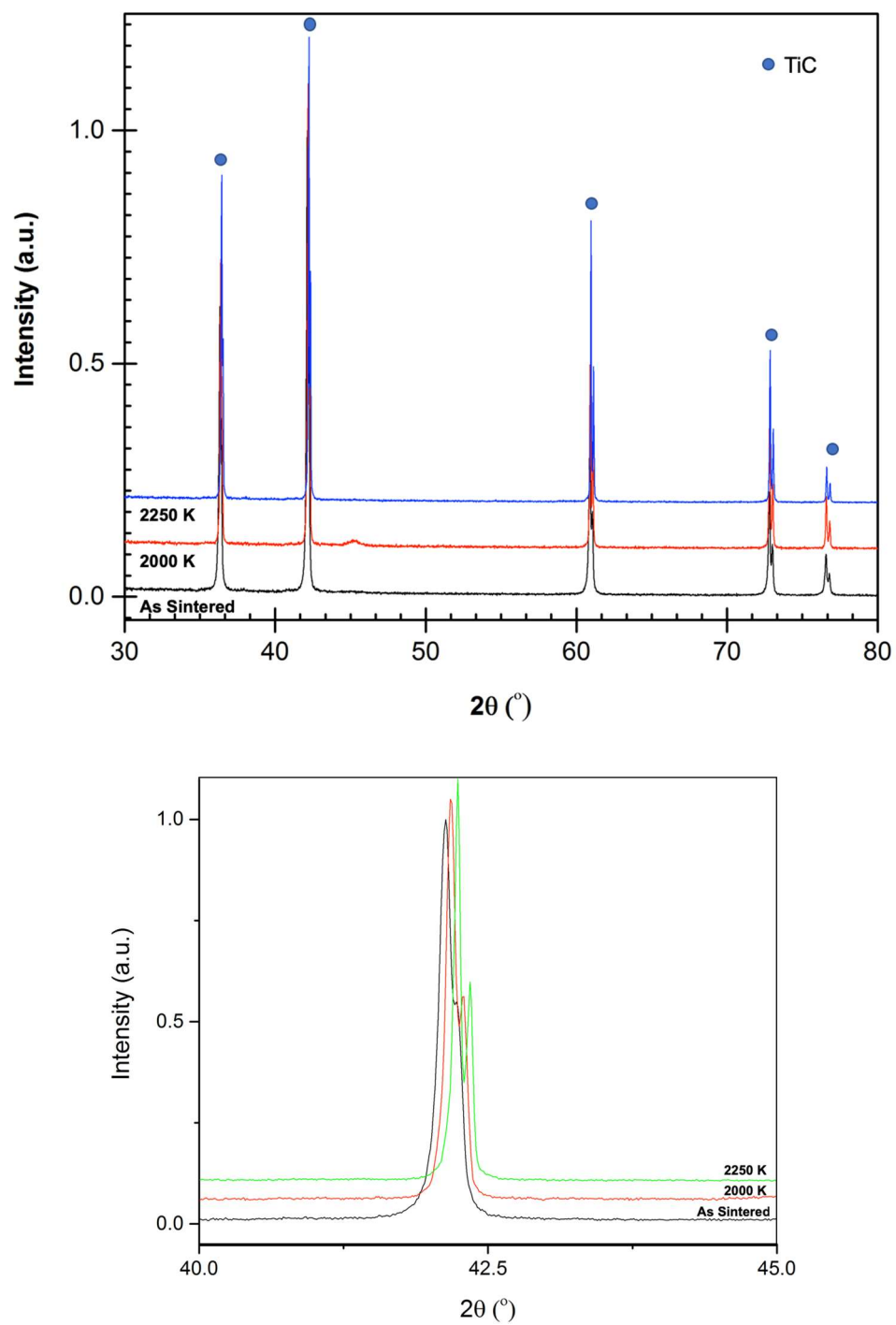


Figure 5.31 XRD spectra of TiC bulk microstructure after exposure to flowing hydrogen at 2000, 2250 K for 120 minutes.

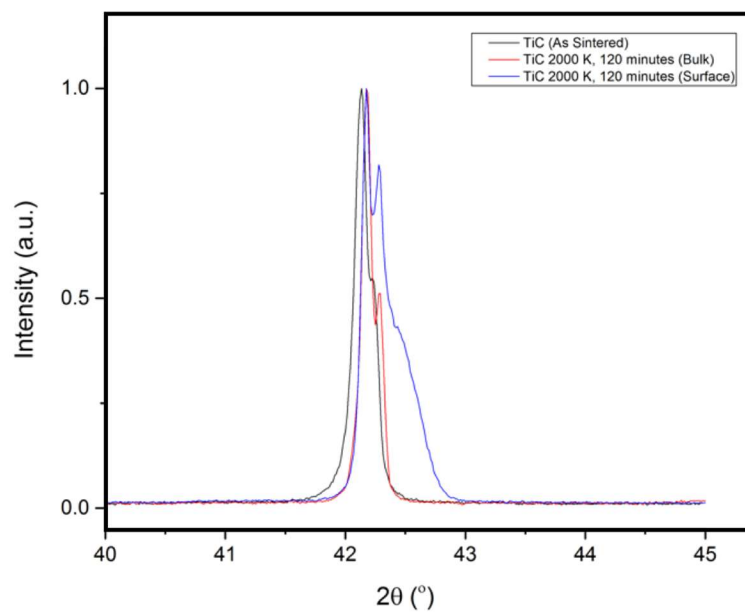
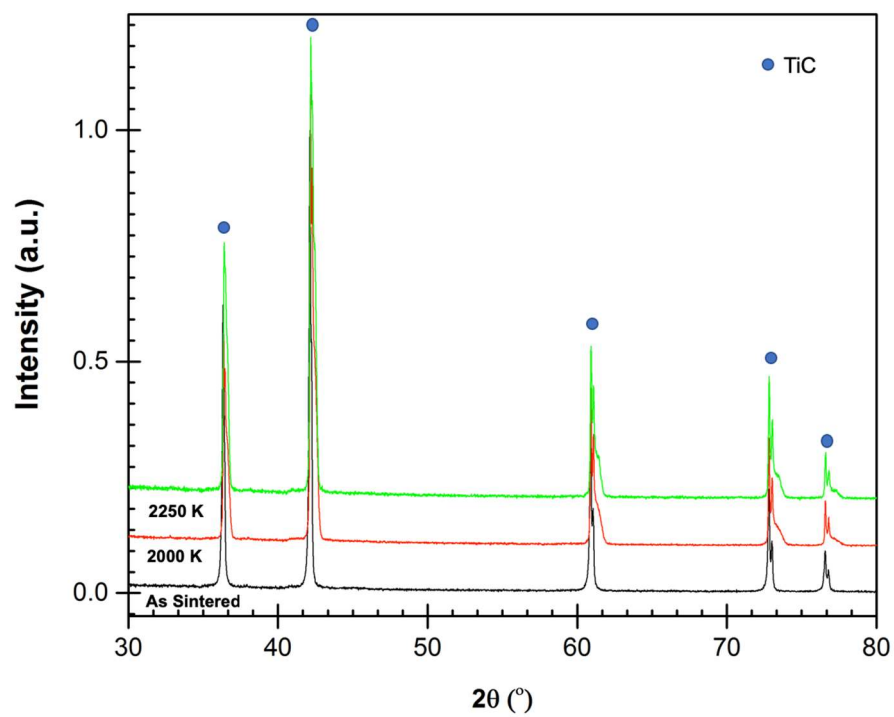


Figure 5.32 XRD spectra of TiC near surface microstructure as sintered and after exposure to flowing hydrogen at 2000, 2250 K for 120 minutes.

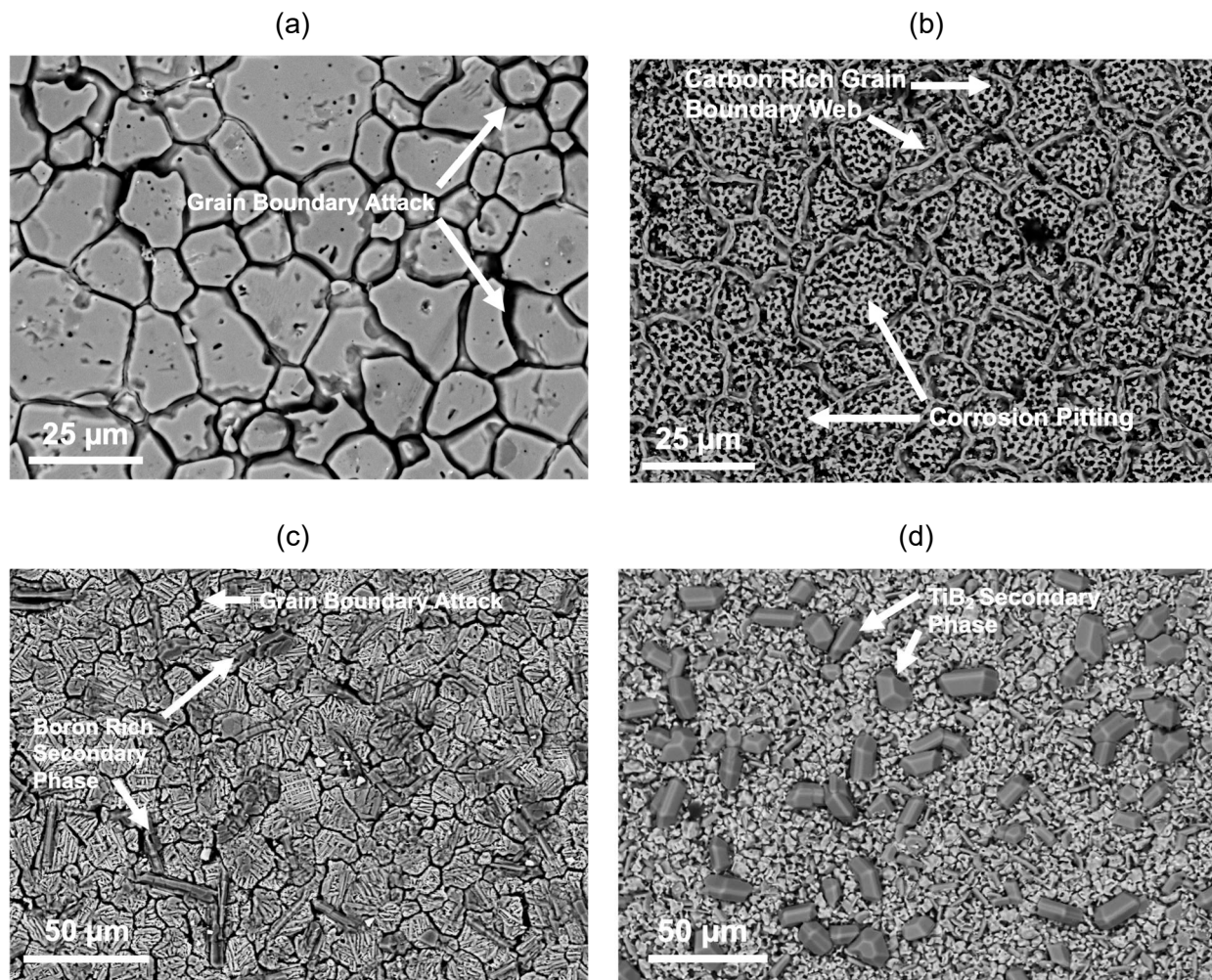


Figure 5.33 Backscatter electron image of TiC surface microstructure after exposure to flowing hydrogen at 2000, 2250, and 2500 K for 120 minutes. At 2000 K, two microstructural regions are dominant: (a) bulk interior region exhibiting grain boundary attack, (b) outer radial region (corresponding to parallel flow) with extensive corrosion pitting of exposed grains and formation of a secondary phase precipitate in the grain boundary. At temperatures above 2250 K, seeding secondary boron rich phases can be identified (c). At 2500 K, large (~15 μm) TiB₂ crystals are present upon the surface microstructure (d).

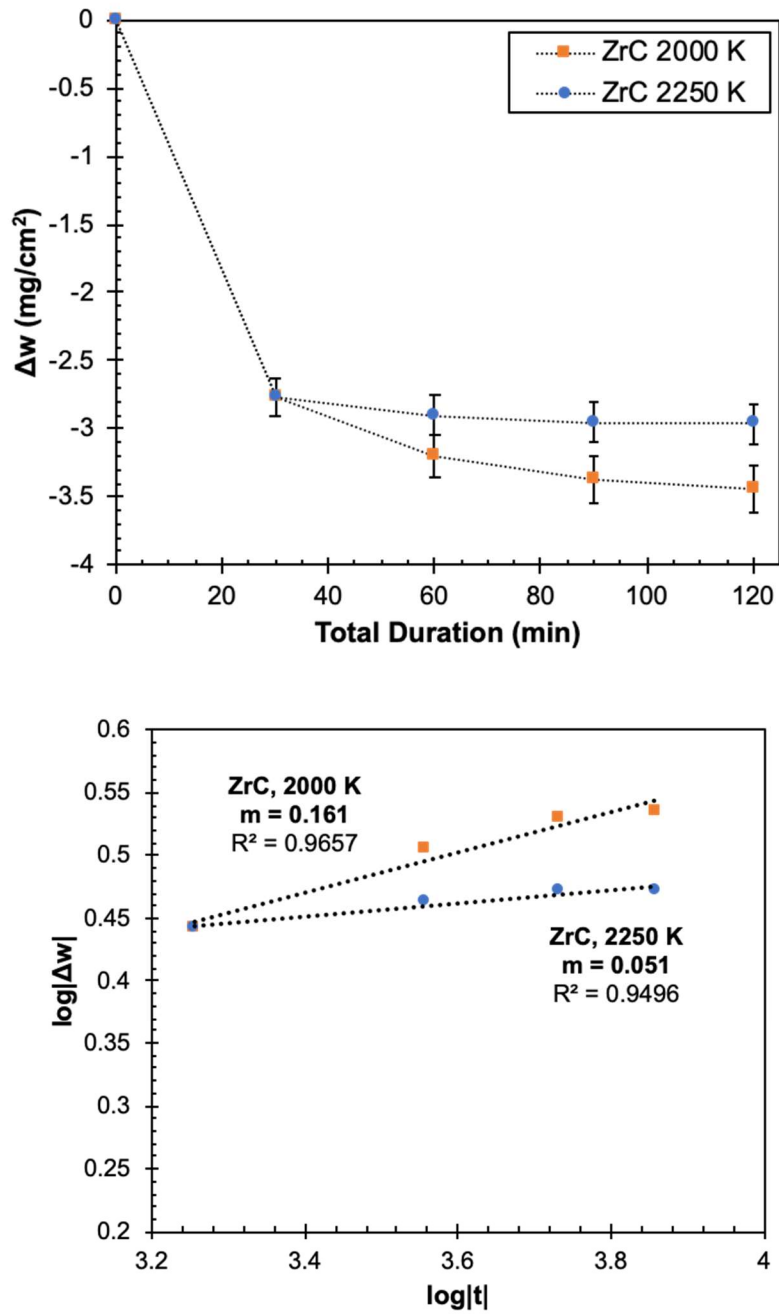


Figure 5.34 Weight change behavior of sintered ZrC after exposure to flowing hydrogen at 2000, 2250 K for 120 minutes.

2000 K rather than 2250 K, which was unexpected. Reduced mass loss at 2250 K was attributed to formation of a protective zirconium diboride phase. XRD performed on the near surface microstructure showed at 2250 K, confirmed the presence of a ZrB_2 phase, while no ZrB_2 phase was present at 2000 K. (figure 5.35)

Initial rapid mass loss may be simply due to loss of impurities intrinsic to the procured powders. SEM micrographs show the presence of oxygen rich impurities which diffuse and precipitate in the grain boundaries at both temperatures. In this case, if initial rapid weight change is due to loss of impurities, ZrC exhibited better overall stability in hot hydrogen than TiC. Analysis of the microstructure shows no evidence of grain boundary attack for the central microstructure of ZrC at 2000 K (figure 5.38). In the outer radial region, extensive intergranular attack or grain boundary attack of sub-grains is present. Similar to phenomena observed in the exposed TiC microstructure, a C rich secondary phase is present in the grain boundaries for each exposure temperature (2000, 2250 K).

The bulk microstructural response of the ZrC monocarbide phase after exposure was investigated using XRD. XRD analysis showed that after exposure, ZrC peaks exhibited a shift in peak position to lower 2θ values for both the bulk and near surface microstructure. This corresponds to a broadening of the unit cell parameter to larger length sizes, which is consistent with strain incurred within the lattice. Lattice strain may be due to microstrain within crystallites or strain caused by compositional gradients, which would be predicted for shifts in the CVC of ZrC. Similar to TiC, the near surface microstructure exhibits an asymmetric broadening to higher 2θ values, suggesting the surface microstructure is highly disordered similar to TiC.

Comparison of Observed TMC Corrosion to the Boundary Layer Diffusion Model

A comparison of total weight loss of high purity SiC, TiC, and ZrC is plotted in figure 5.38. At 2000 K, SiC exhibited more stable weight change behavior than TiC and ZrC when comparing absolute mass losses. When comparing specific mass loss, ZrC exhibited the most stable response in a hydrogen environment. At temperatures greater than 2000 K, TiC and ZrC exhibit much lower mass losses than SiC, showing decomposition and removal in hydrogen exhibits a much lesser temperature dependence than SiC.

In SiC, the volatilization rate of the sample material in flowing hot hydrogen can be represented with a linear time dependence. However, because of the wide range of stoichiometry which satisfies the monocarbide phase of TMCs (figure 5.39), it has been postulated that volatilization/vaporization behavior in hot hydrogen will initially deviate from linearity due to

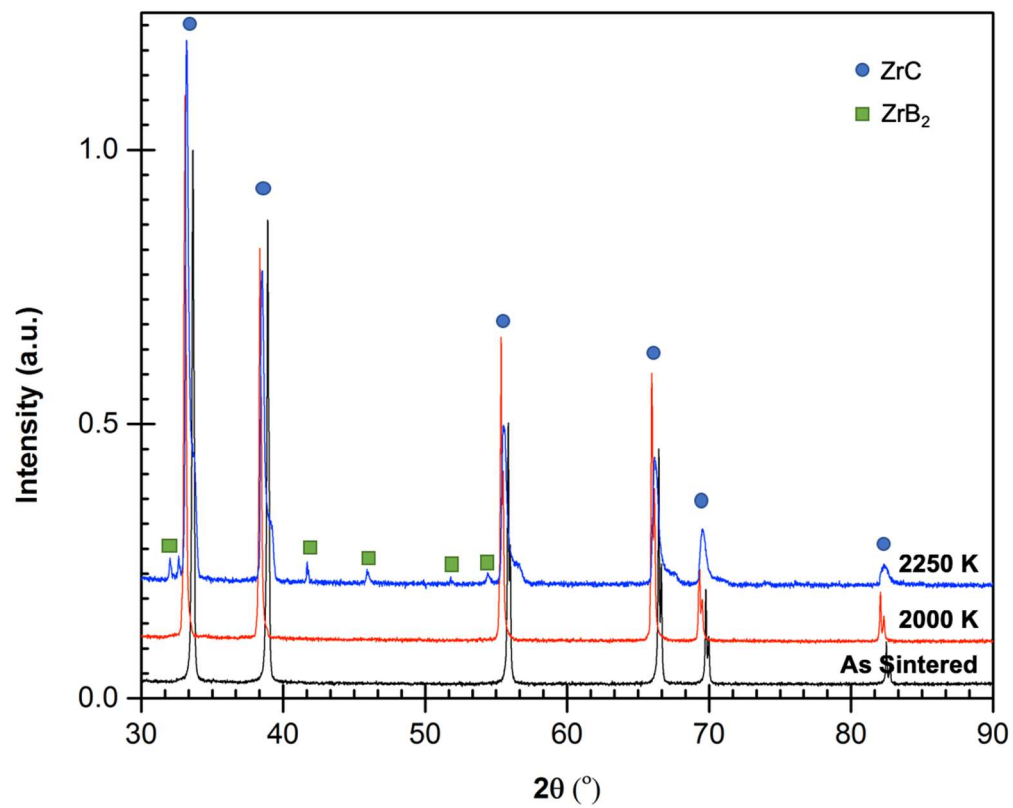


Figure 5.35 XRD spectra of ZrC near surface microstructure as sintered and after exposure to flowing hydrogen at 2000, 2250 K for 120 minutes.

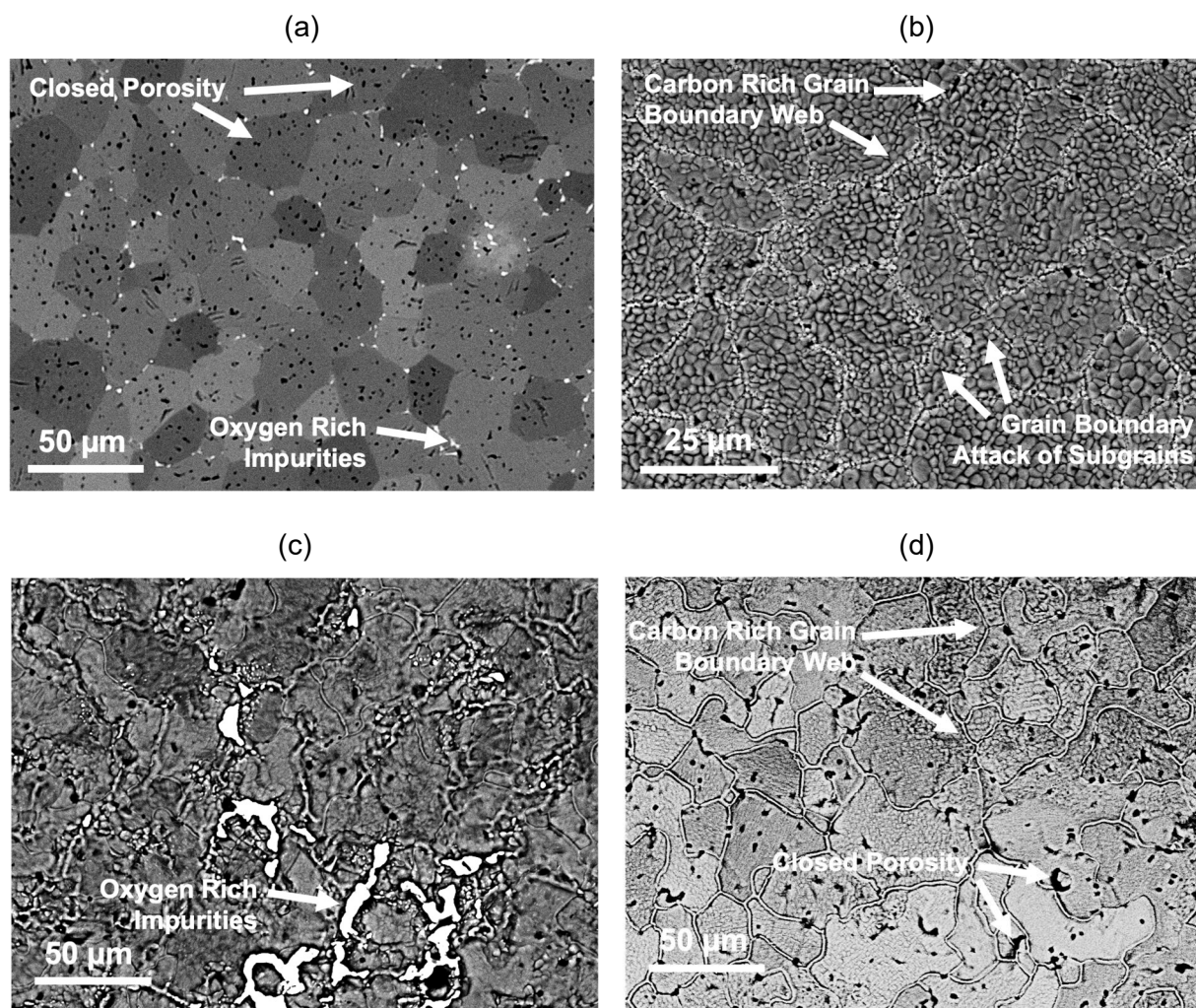


Figure 5.36 Backscatter electron image of ZrC surface microstructure after exposure to flowing hydrogen at 2000 and 2250 K for 120 minutes. At 2000 K, the exposed surface microstructure primarily shows evidence of grain boundary attack of ZrC sub grains and precipitation of a C rich secondary phase in the grain boundary web (b). At both temperatures, agglomeration of oxygen rich phases in the grain boundaries show evidence of diffusion of impurities from the sample bulk to the surface (a,c) can be identified. At 2250 K, the C-rich precipitates form a continuous phase in the grain boundaries (d).

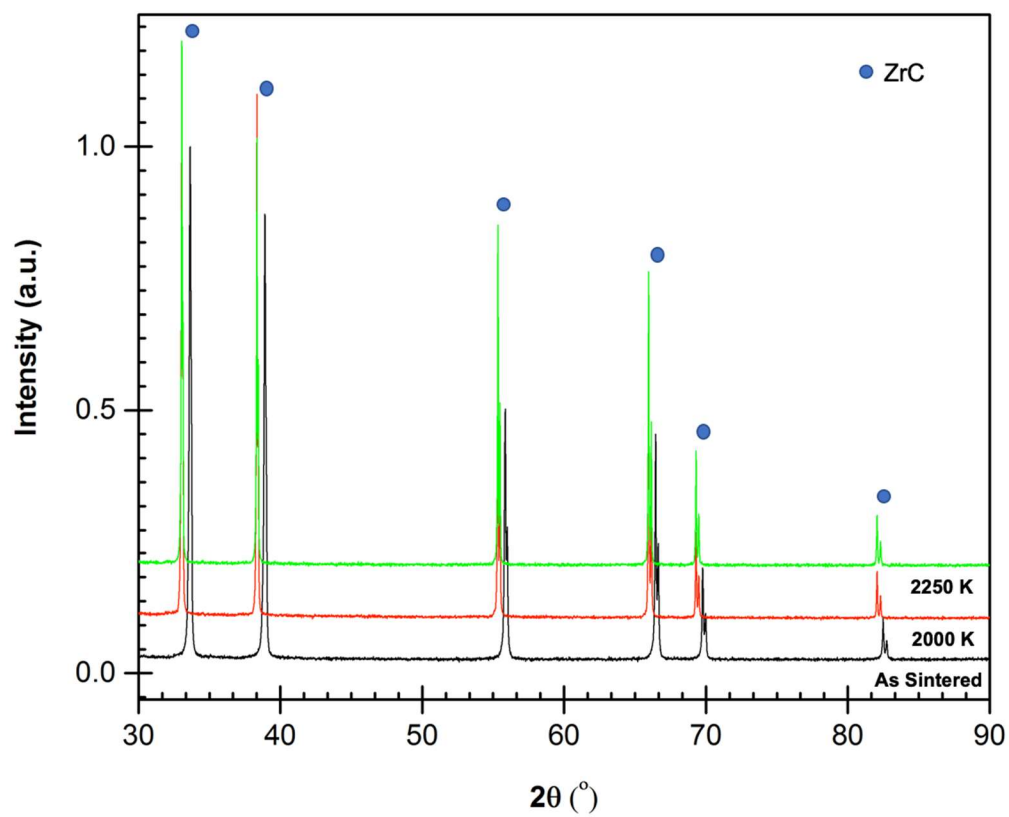


Figure 5.37 XRD spectra of ZrC bulk microstructure after exposure to flowing hydrogen at 2000, 2250 K for 120 minutes.

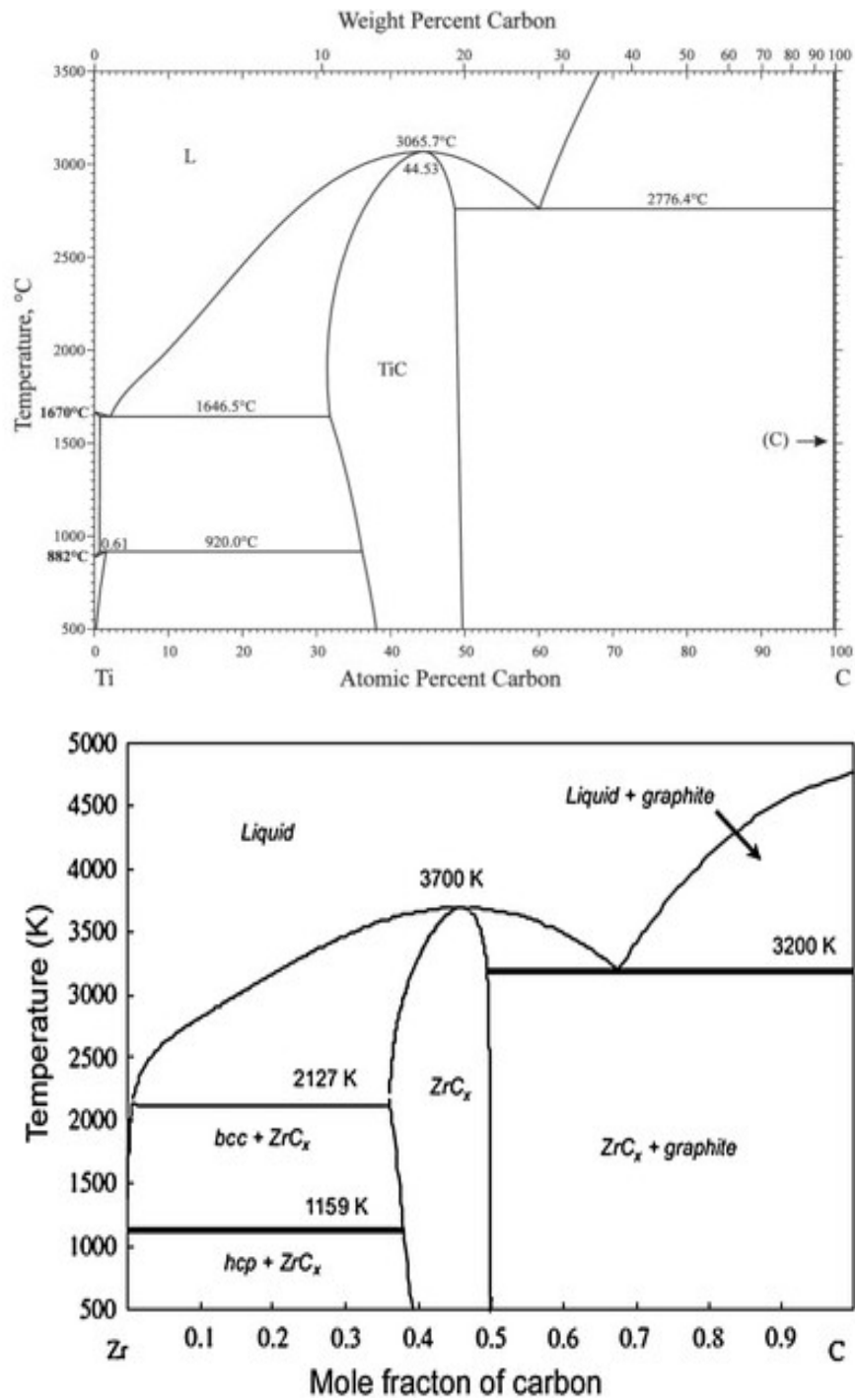


Figure 5.38 Phase diagrams of TiC and ZrC showing wide range of stoichiometry which satisfies the monocarbide phase [96, 97].

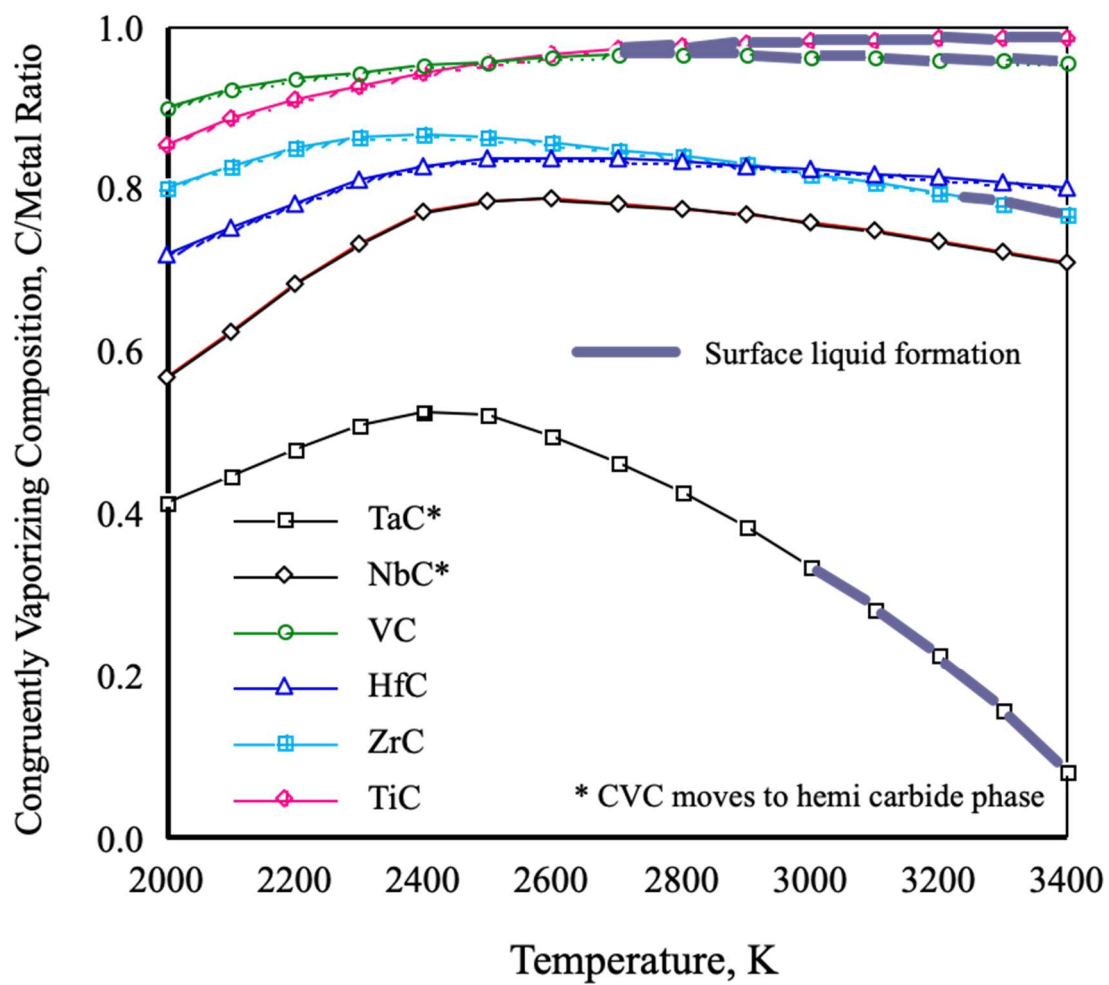


Figure 5.39 Predicted congruent vaporization composition (CVC) of selected transition metal carbides in a 1 atm hydrogen environment [88].

incongruent vaporization of carbon and metal from the sample surface. Butt et. al. has calculated predicted congruently vaporizing compositions (CVCs) of selected transition metal carbides using modified Langmuir models [73]. Depending on the initial composition of fabricated TMC sample coupons, it is expected that a shift in composition to values between 0.8 – 0.9 is expected for exposure temperatures of 2000, 2250 K. If there is an initial incongruent rate of free metal and carbon vaporizing from the surface, these phenomena will result in non-linear mass change until the CVC is achieved, at which a steady state is expected. The transient until steady state rate is achieved will be dependent upon the formation of a bulk composition which supports the equilibrium diffusion rates to supply the metal and carbon atoms necessary for composition at the surface which allows for congruent vaporization of the material.

Observed mass loss rates of TiC and ZrC in hydrogen environments at 2000 and 2250 K are compared to predicted mass losses in figures 5.41 and 5.42. No agreement of observed corrosion dependence of the TMCs in hydrogen with the boundary layer diffusion limited gas transport model. When testing TiC and ZrC, non-linear weight change behavior was observed. This behavior is anticipated from incongruent vaporization theory of TMCs in high temperature environments, however no conclusive evidence could be obtained to quantify a shift in the surface C:M ratio of TiC and ZrC in flowing hydrogen. Thermodynamic calculations predicted equilibrium mass fluxes assuming an ideal monocarbide 1:1 C:M ratio. It was expected that the response of TiC and ZrC in high temperature flowing hydrogen would preferentially lose carbon to form a sub-stoichiometric C:M ratio monocarbide at the exposure surface, which affects the overall activity of the reactant solid and equilibrium partial pressures of volatile gas species. However, velocity TiC exhibited no dependence of corrosive mass loss rate with change in gas velocity. Due to the independence of corrosive weight loss with respect to gas stream velocity, corrosion phenomena may be better modelled with a surface reaction limited model or internal mass transfer model. TMCs may transition to a mass transfer limited process at higher exposure temperatures. XRD of tested coupons showed a shift in bulk microstructure ZrC peak positions to lower 2theta values, which is consistent with carbon loss. However, TiC exhibited the opposite behavior, which is expected in the case of preferential loss of metal from the carbon surface. For TiC, peak shifts to higher 2 theta was accompanied by peak sharpening, therefore, sintering of the bulk microstructure upon high temperature exposure is more likely the cause of observed peak changes. Other contributions to the sublinear corrosion behavior could be due to preferential reaction of the TMC with B-containing impurities in the gas stream. Formation of transition metal borides, TiB₂ and ZrB₂ were attributed to forming a passivating secondary phase on the TMC surface which suppressed observable corrosion.

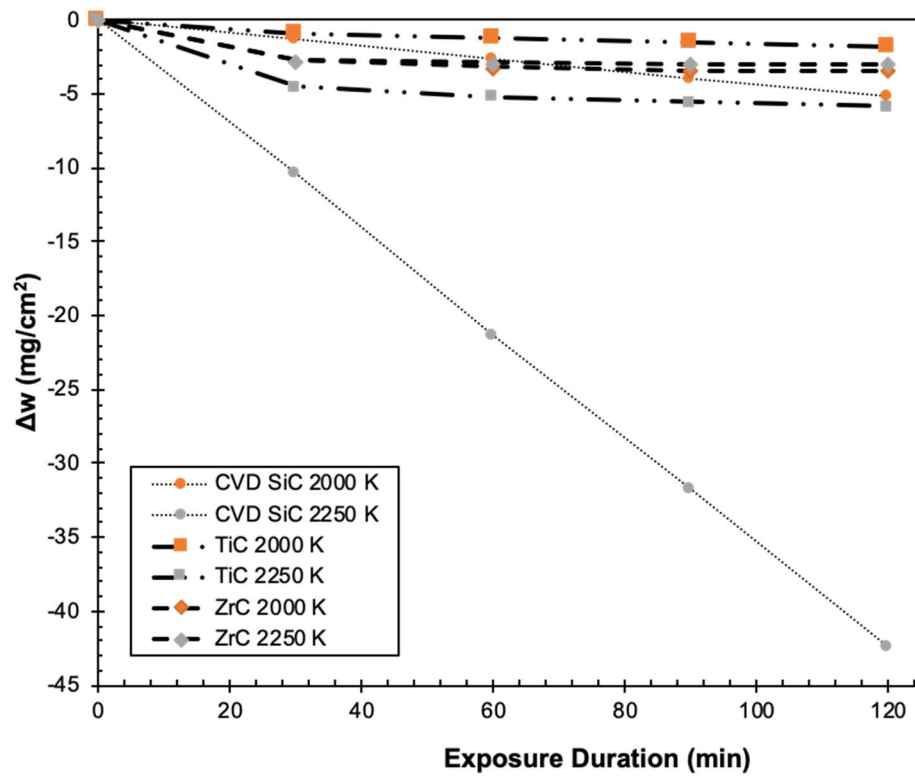


Figure 5.40 Comparison of total mass losses of SiC, TiC, and ZrC after exposure to hydrogen for 120 minutes at 2000 and 2250 K.

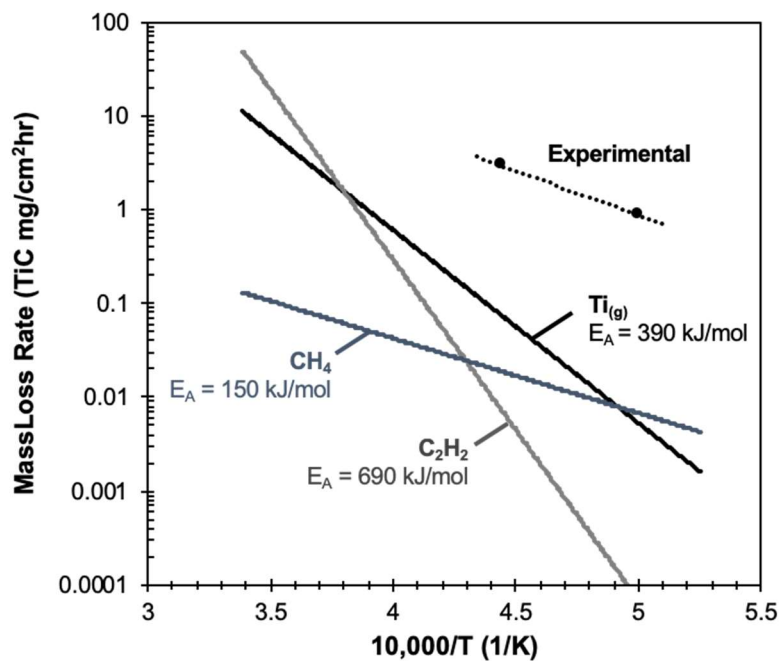


Figure 5.41 Comparison of mass loss behavior observed of TiC with mass losses predicted by the boundary layer diffusion limited model

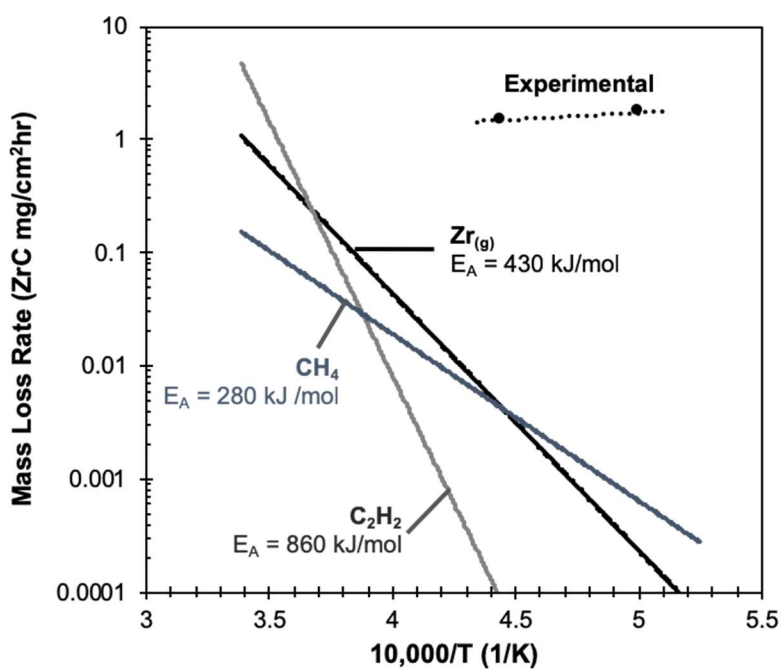


Figure 5.42 Comparison of mass loss behavior observed of TiC with mass losses predicted by the boundary layer diffusion limited model

While TMCs exhibited contamination from BN in the gas stream, SiC samples did not show evidence of interaction with BN. Figure 5.43 exhibits the predicted thermodynamic of SiC in hydrogen with various levels of BN impurities. For low BN impurity concentrations (10^{-5} mol%), free Si vapor and CH₄ are the primary predicted corrosion products. For concentrations exceeding 10^{-5} mol%, BN impurities in the hydrogen gas are predicted to react to form BH₂ and N₂ gas. SiC is compatible with N₂ gas. However SiC is completely incompatible with BH_x species can react to form SiB₆ and B₄C (Eq. 5.7):



Therefore, with too high addition of BN impurities into the gas stream, SiC corrosion will increase due to interaction with BH_x.

Discussion of Results and Recommendations for Future Work

Coupons of high density (>95%TD) TiC and ZrC were sintered for hot hydrogen testing using spark plasma sintering. Both TiC and ZrC exhibited sublinear weight loss behavior during 2000 and 2250 K thermal cycling in flowing hydrogen. Bulk TiC behavior showed evidence of sintering, as seen by peak sharpening and shift in peak heights to higher 2theta values. Surface microstructure showed disordering and formation of a boride secondary phase above 2250 K. Near surface TiC microstructures at 2000 K exhibited grain boundary attack in the central region of the coupon and extensive porosity, corrosion pitting in the outer radial region. Corrosion in the central region may have been suppressed due to pick up of corrosion products in the gas stream. XRD analysis of the bulk ZrC microstructure did not show evidence of secondary phase formation, ZrC peaks shifted towards lower 2theta values after hot hydrogen exposure which corresponds to a shift in the lattice parameter to larger values. ZrC exhibited higher mass losses at 2000 K than 2250 K, this was due to the formation of ZrB₂ on the surface of samples. ZrB₂ is more stable in hydrogen than ZrC resulting in a passivating layer on the surface. Both ZrC and TiC exhibited the formation of a carbon rich phase in the sample grain boundaries. Initial rapid weight loss of ZrC in flowing hydrogen maybe due to loss of impurities intrinsic to the feedstock powders.

Although ZrC and TiC exhibited nonlinear weight change behavior, at 2000 K, TiC and ZrC exhibited similar weight losses as CVD SiC after 120 minutes of exposure time. At temperatures greater than 2000 K, ZrC and TiC exhibited much lower mass losses than CVD SiC. This may suggest that the activation energy of ZrC and TiC maybe lower than that of the intrinsic value of SiC. However, due to boron pick up from the gas stream and suppression of the corrosion reaction, future work should be undertaken to identify a boron getter to eliminate impurity

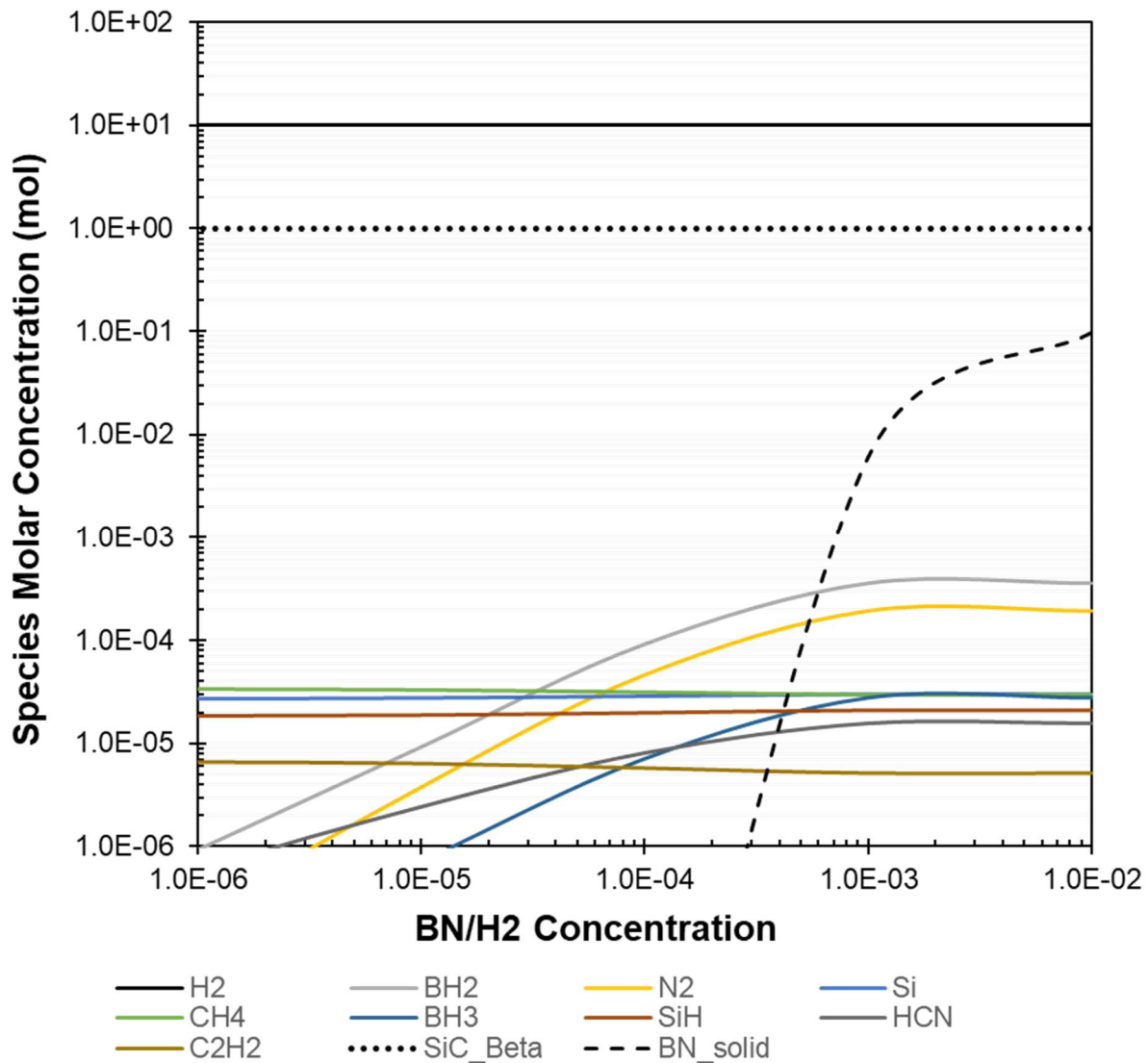


Figure 5.43 Predicted thermodynamic stability of SiC in 2000 K hydrogen with various levels of BN contamination.

interaction with fabricated samples. ZrC and TiC may degrade due to incongruent vaporization, some evidence obtained via XRD suggests a change in the lattice parameter (corresponding to defects in the carbon or metal lattice) however, no conclusive evidence was found through these initial scoping experiments. ZrC and TiC may be higher performing structural fuel matrix candidates for higher temperature exposure than SiC.

In order to confirm if the controlling mechanism for TMC degradation in hot hydrogen is due to incongruent vaporization from the sample surface, the following are suggested:

- 1. Identification of a fabrication pathway to sinter near theoretical density, high purity samples with uniform composition (stoichiometry) from the sample surface to the bulk or characterization of the depth dependence of TMC stoichiometry. This includes optimization of sintering parameters and identification of high purity powder feedstock vendors.*
- 2. Initial characterization of as fabricated sample coupons and tested sample composition to understand both light element (B,C,O,N) and heavy element (transition metals and other impurities) purity and initial overall stoichiometry. Light element analysis via time of flight mass spectrometry (ToF-MS) and optical emission spectroscopy (OES) are suggested. Tested samples should aim to understand differences in the surface and bulk microstructure. Elemental analysis using ToF-MS or OES may be coupled to complimentary characterization techniques glowy discharge optical emission spectroscopy (GDOES) or grazing incidence x-ray diffraction (GIXRD) to characterized depth dependence of C:M ratio in the case of changes in CVC.*

CHAPTER SIX - CONCLUSIONS

The purpose of this work was to evaluate the corrosion behavior of refractory carbide: SiC, TiC, and ZrC materials in NTP relevant environments. This was undertaken through thermodynamic modelling and the thermal cycling of high purity, high-density material coupons in flowing hydrogen environments at temperatures relevant to NTP (2000 – 2500 K) to understand intrinsic material performance. Thermal cycle and duration testing of SiC coupons fabricated via the NITE method was also completed for a range of temperatures (1173 – 2500 K) and compared to intrinsic SiC performance. In order to achieve the desired outcomes of this study a complimentary approach of mass change measurements and microstructural evaluation was performed.

It was predicted that SiC would have the lowest stability in a pure hydrogen environment, while ZrC would have the highest stability. Thermodynamic predictions predicted decomposition of the refractory carbide into free metal and free carbon with subsequent vaporization of the free metal from the surface and interaction with free carbon to form hydrocarbons. The most stable hydrocarbon was predicted was methane at low temperatures which transitioned to acetylene at high temperatures. The transition temperature varied with each material. It was found that SiC exhibited acceptable compatibility with hydrogen up to temperatures of approximately 2250 K. Although, SiC experiences active corrosion in the flowing hydrogen environment, material degradation was within heritage limits and no formation of undesirable corrosion products occurred. For all temperatures, SiC exhibited a linear weight change dependence on flowing hydrogen, which is consistent with volatilization kinetics. TiC and ZrC exhibited superior weight change behavior than SiC at temperatures exceeding 2250 K. Weight change behavior was sublinear, which was expected for the group IV, V transition metal carbides due to their wide range in stoichiometry. However, mass loss rate was not observed to be dependent upon gas stream velocity, suggesting that the reaction may be surface reaction controlled or internal mass transfer limited. When the microstructure was evaluated in detail, it was found that at 2000 K the surface microstructure became highly porous and exhibited the formation of a C-rich precipitate in the grain boundaries. No evidence of secondary phase formation was obtained from evaluating the near surface XRD spectra at low temperatures, however asymmetric peak broadening (to higher 2θ values) was observed, which is indicative of heterogeneous strain. Above 2000 K, the carbide surface was highly reactive to react with gas stream impurities, however, no evidence of undesirable hydride formation was observed. For high performance NTP systems, TiC and ZrC could be desirable alternative matrix candidates to allow for longer operating lifetimes and the potential for higher operating temperatures compared to CVD SiC.

NITE SiC exhibited much higher mass loss in flowing hydrogen than pure CVD SiC and exhibited sublinear weight change behavior when thermal cycled at 2000, 2250 K. This was attributed to the preferential attack of sintering additives (Al_2O_3 and Y_2O_3), which were observed to rapidly volatilize from the surface of SiC to leave behind a very porous microstructure which increases sample surface area, pathways for further hydrogen attack. Rapid volatilization of sintering additives resulted in a reduction of the apparent activation energy of NITE SiC (290 kJ/molK) when compared to CVD SiC (370 kJ/molK). After exposure to 2250 K, above the Al_2O_3 -SiC- Y_2O_3 eutectic formation temperature, the secondary eutectic phase appeared to be mobile and agglomerated rather than existing uniformly throughout the microstructure. At temperatures above 2250 K, sintering additives were no longer compatible with the SiC matrix and reacted to form Y-rich secondary phases. From this study of CVD SiC as a protective coating is acceptable to temperatures up to 2250 K. It is suggested, due to the microstructural instability of NITE SiC and high mass losses observed under thermal cycling conditions, uncoated NITE SiC should be limited to use temperatures of less than 2000 K. Development of high performance barrier coatings and identification of alternative high temperature sintering additives may allow for the NITE SiC fabrication method to be useful for high performance NTP applications.

From this study, it was found that ZrC was the most stable material candidate tested, followed by TiC, then SiC. SiC performance is still acceptable for temperatures up to 2250 K, making it a good candidate for midband protective coatings of the fuel or as a structural component at intermediate temperatures. NITE SiC exhibited high mass losses for exposure temperatures of 2000 K and higher. It is recommended NITE SiC not be utilized as an uncoated fuel matrix for any exposure temperatures exceeding 1950 K. NITE SiC as currently fabricated should not be operated above 2250 K due to instability of the SiC matrix with Al_2O_3 and Y_2O_3 additive oxides in a reducing environment. For future application of RCs as alternative NTP fuel matrix candidates, it is suggested that future testing should confirm acceptable chemical compatibility of the RC and relevant sintering materials in a reducing, high temperature environment. For the proposed fuel system evaluated in this study, the effect of chemical compatibility of the fuel matrix with the hydrogen propellant, relevant sintering aids or coatings, and dispersed fuel particles may play the limiting role in total fuel lifetime capability.

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APPENDICES

Appendix A. Survey of Fuel System Options for Low Enriched Uranium (LEU) Nuclear Thermal Propulsion

(K. Benensky et. al. Nuclear and Emerging Technologies for Space Conference 2017)

Introduction

A non-chemical propulsion technology, nuclear thermal propulsion uses the energy released from fission to directly heat a propellant, which is expanded through a nozzle to provide 100 – 2,200 kN thrust. Use of high operating temperature nuclear fuel and hydrogen propellant allows for specific impulses (I_{sp}) of 800 – 950 s to be achieved. These attributes of high thrust levels and I_{sp} allow for reduced trip times and increased cargo payloads for interplanetary missions. Historic engine designs have been optimized to meet past performance needs by minimizing engine sizes for a given thrust level using high enriched uranium (HEU) fuel. However, recent studies have shown that low enriched uranium (LEU) engine designs containing less than 20 wt% ^{235}U content, are capable of achieving comparable performance to HEU engine designs [8, 11, 13, 98]. Use of LEU fuel has the potential to reduce the high maintenance cost and perceived political hurdles of developing nuclear thermal rocket systems traditionally associated with high enriched uranium (HEU) fuel systems. Further, LEU nuclear thermal rocket (NTR) engine designs can promote future development and licensing of NTRs for private industry. Additionally, the use of modern manufacturing technologies and design techniques, such as spark plasma sintering (SPS), melt infiltration, reinforced ceramic matrix composites, etc. can be leveraged to facilitate the manufacture of more desirable microstructures or enable manufacture of new classes of fuel systems, which may be specifically advantageous for use in a LEU NTR engine. The purpose of this paper is to survey material candidates for LEU NTP fuel systems in order to guide down selection of the most viable structural matrix candidates based on selective material properties and known material performance under known engine operating conditions. Material candidates which best satisfy the needs of operation within a nuclear thermal rocket environment are assessed using infinite lattice calculations.

Proposed NTP fuels must enable the demonstrated performance benefits of NTRs developed in historic programs. Therefore, nuclear fuel systems must allow for operating temperatures in excess of 2500 K and resist interaction with the corrosive hydrogen propellant. Due to the dependence of core power (and mechanical loading profiles) on fuel system geometry and mass, fuel elements need to resist fuel mass loss and retain strength and structural stability for the range

of operating conditions during the rocket lifetime. High fuel element operating temperatures may result in vaporization at the surface of the fuel system or cause thermal stresses between the fuel matrix and relevant interfaces such as protective claddings, coatings, or dispersed fuel particles. Fuel elements must be able to survive thermal shock incurred during start up for a single burn and recover from previous use to upkeep performance during multiple restarts of the engine. Key attributes of fuel systems for an LEU NTR must enable:

- *High operating temperature: low vaporization, thermodynamic stability*
- *Criticality: low thermal neutron absorption, good moderating power*
- *Chemical compatibility with coolant, fuel particles, and relevant claddings*
- *Mechanical/structural stability over a wide range of operating temperatures: predictable mechanical properties to accommodate thermal stresses or changes in physical properties with temperature, irradiation*

The following section presents a literature review of high temperature materials to support nuclear space applications and known fuel performance under limiting nuclear thermal propulsion applications.

Literature Review

Very few materials can withstand the operating conditions necessary for operation of a nuclear thermal rocket. At the minimum, LEU fuels must have high melting temperature and low neutron absorption cross sections to enable maximum temperature during operation and allow for critical geometries to be attained. Material candidates that are incompatible with the hydrogen propellant will require protective coatings to protect against chemical attack. Only few elements exist with a melting temperature above 2700 K: Ir (2719 K), Nb (2740 K), Mo (2890 K), Ta (3290 K) Os (3310 K), Re (3438 K), W (3695 K), and C (4300 K) [45]. These elements are mostly transition metals, with the exception of carbon, which as graphite sublimates at 4000 K in a vacuum [45]. High temperature compounds with melting temperatures above 2700 K include transition metal and refractory carbides, oxides, borides, silicides, sulfides, phosphides, and intermetallides. Of these applicable high temperature materials, graphite [2, 23], transition metals [27, 33], and transition metal carbide based fuel systems [40] have been developed and tested in past NTP development programs of the United States.

High Melting Temperature Elements: Graphite and Transition Metals

Fundamental Considerations for Graphite Fuel Systems to Support NTP

Compared to other materials, graphite offers the ability for exceptionally high operating temperatures, good high temperature strength, relative ease in fuel form manufacture, low thermal neutron absorption, and a large established irradiation database/operational experience. Graphite based fuels were the first fuels developed for NTP in the United States through the Nuclear Engine for Rocket Vehicle Application (NERVA)/Rover program. Throughout the program, fuel forms evolved from dispersed UO_2 or UC_2 particle impregnated graphite plates to extruded hexagonal fuel elements containing a dispersed uranium-zirconium carbide, $(\text{U,Zr})\text{C}$, fuel web with coolant channels for hydrogen flow [23]. The NERVA/Rover program was the only program to test fuels in NTP prototype engines. Over 20 test reactors containing graphite based fuels were ground tested throughout the duration of the program (1955 – 1972) [2]. Graphite based fuels are the only fuel type that has been tested in a fully assembled reactor core with the prototype conditions of a nuclear thermal rocket.

The key advantage of graphite-based fuels for LEU NTP application is the low thermal neutron absorption cross section and high scattering cross section of carbon. This allows the structural graphite matrix to also function to moderate the neutron flux within the core. Graphite based fuels have acceptable thermal conductivity and high temperature strength, which allows for the reduction of local hot spots and reliable mechanical response during operation. Due to the extensive database of operating experience, the failure modes of graphite based fuels are well known and is reviewed elsewhere [23-26]. The largest risks associated with developing graphite based fuel systems is associated with the incompatibility of graphite with the hot hydrogen propellant, which alters the reactor power profile during operation and degrades the structural integrity of the matrix. Exposed graphite must be coated using protective coatings/claddings to prevent exposure to the hot hydrogen environment and subsequent corrosion. Minimizing incurred thermal stress and dimensional instability of graphite fuels is key to maintain coating integrity.

Fundamental Considerations for Transition Metals to Support NTP

Six transition metals have been identified and tested as high temperature materials for nuclear space applications: Ir, Nb, Ta, Re, Mo, and W [99-102]. Transition metals which can withstand such high temperature operation and are extremely heat and wear resistant are often referred to

as refractory metals. The advantages of refractory metals are their capability for high temperature operation, high temperature strength, high thermal conductivity, and high ductility at the operating temperatures desired for nuclear thermal propulsion. When selecting refractory metals for LEU nuclear fuel systems neutron cross section, high temperature stability, and chemical compatibility are the most important parameters to consider. Secondary material properties that should be considered includes the evaluation of the ductile to brittle transition temperature (DBTT) for body centered cubic (BCC) alloys. High DBTT increases difficulty in fuel manufacture and reduces a materials ability to resist crack propagation during operation. Low temperature irradiation and hydrogen embrittlement is known to increase the DBTT and could degrade the mechanical response the fuel during re-start conditions.

Iridium is a high melting temperature element from the Platinum group. Iridium is extremely inert and typically used for encapsulating the power sources for radio thermoelectric generators (RTGs) [103] . However, its high natural neutron absorption cross section of 425 b makes it unsuitable as a structural material in the active core of a NTR [46].

The advantage of Nb and Ta compared to other refractory metals are their low ductile to brittle transition temperature, below room temperature (298 K) which is desirable for fuel fabrication and to ensure ductile fuel response over the range of operating temperatures along the fuel length [102]. These metals can maintain their strength for very high temperature operating conditions and have been investigated as structural components for space power systems. However, at temperatures below 800°C (1073 K), Nb and Ta easily uptake hydrogen and have high hydrogen solubility [104]. Fuel operating in low temperature regions near the inlet is susceptible hydrogen embrittlement during operation and the total length of the fuel is susceptible to hydrogen uptake during core cooldown. Hydrogen ingress is not desired as it reduces metal ductility, may also result in the formation of low melting temperature metal hydrides, and affects the neutronic power profile during operation or restart. At very high operating temperatures, Ta and Nb are incompatible with UO_2 and UC fuel. Ta and Nb tend to reduce UC fuel and form refractory metal carbides. While UO_2 is stable within Ta and Nb, the metals will interact with free oxygen produced during high temperature UO_2 operation to form lower melting temperature oxides [102, 105, 106]. It has been suggested through previous studies that high temperature coatings such as W may be acceptable to mitigate the interaction, however, use of W coatings will introduce a neutronic penalty [102].

Of the transition metals, only Mo, W, and Re are thought to be suitable matrix materials for NTP fuel systems. Mo and W are BCC type alloys with a high DBTT, making these materials more brittle and difficult to manufacture compared to Nb and Ta. Rhenium has a hexagonal close packed (HCP) crystal structure and is typically alloyed with Mo or W to produce a more ductile material response. Mo and W have undergone extensive development and separate effects testing [27, 41] (high temperature irradiations, hot hydrogen testing, thermal cycling, and thermal shock), while Re based fuels have only been demonstrated to be compatible with UO_2 to temperatures of ~ 2500 K [107]. Re has a high thermal absorption cross section for all stable isotopes and is not a good candidate for LEU NTP despite its desirable ductility. Additions of Re should be limited when used. From 1962 – 1968, General Electric's 710 Gas Reactor program developed and tested Mo and W metal matrix fuels with distributed uranium dioxide (UO_2) or uranium nitride (UN) fuel particles [27]. Ultimately, it was observed that the vapor pressure of Mo became significant at 2470 K, limiting its expected performance as an alloying element [31]. Due to the higher melting temperature and better thermal stability of tungsten in the hydrogen environment, later fuel development focused on W-based fuels.

The development of W-matrix ceramic-metallic (cermet) fuels addressed the specific design challenges encountered in the Rover/NERVA program. Tungsten is compatible with the hydrogen propellant and exhibits superior high temperature strength and endurance [108]. The main drawbacks of W-cermet fuel are high thermal neutron cross section and high DBTT, which results in difficulty in the manufacture and machining of full length fuel elements. Although W has a high thermal absorption cross section, cermet fuels do allow for higher volume loadings of fuel within the matrix without significantly compromising the fuel's mechanical integrity. Most reference cermet engine designs use fuel loadings of 60 vol% within the matrix to compensate for the high natural thermal absorption cross section of W. In order to maintain structural integrity of graphite composite fuels, fuel loading must be limited to 35 vol% or less [23]. LEU NTR designs using a W-cermet fueled core have been demonstrated, but require the use of external moderating elements and enrichment of natural W in the W-184 isotope. W-cermet fuels have been the subject of high temperature irradiation and hot hydrogen testing through past program developments, which has lead to a good understanding of fuel behavior and potential failure pathways [24, 31, 33]. The largest risks associated with the operation of W-cermet fuel systems is attributed to the vaporization and migration of UO_2 fuel during high temperature operation, which leads to loss of reactivity and structural integrity of the fuel system [33]. Modern manufacturing methods such as via spark plasma sintering (SPS) have demonstrate the

production of tungsten elements close to theoretical density, which is expected to assist in the retention of fuel during operation [34, 109].

High Melting Temperature Compounds: Refractory Carbides

Figure A.1 demonstrates all elements and high temperature compounds with melting temperatures above 2500°C, which include transition metal and refractory carbides, oxides, borides, silicides, sulfides, phosphides, and intermetallides. Silicides, phosphides, and sulfides have too low a melting temperature (< 3000 K) and are not capable of achieving high operating temperatures necessary for comparable performance to reference LEU NTR designs. Boron and rhenium containing compounds will function as neutron absorbers within the reactor core and will not allow for the critical design of a LEU NTR. High melting temperature oxides, nitrides, and carbides are capable of high temperature operation with low thermal neutron absorption cross sections. Oxides are not recommended in the reducing hot hydrogen environment due to high expected vaporization rates and high temperature thermodynamic instability [84]. While both carbide and nitride compounds offer hot hydrogen compatibility, refractory carbide compounds offer the highest known melting points and superior high temperature stability with lower thermal neutron absorption cross sections. Of all known high temperature compounds, carbides have highest potential for use in a LEU NTR due to their low absorption cross sections, high temperature stability, and hot hydrogen compatibility.

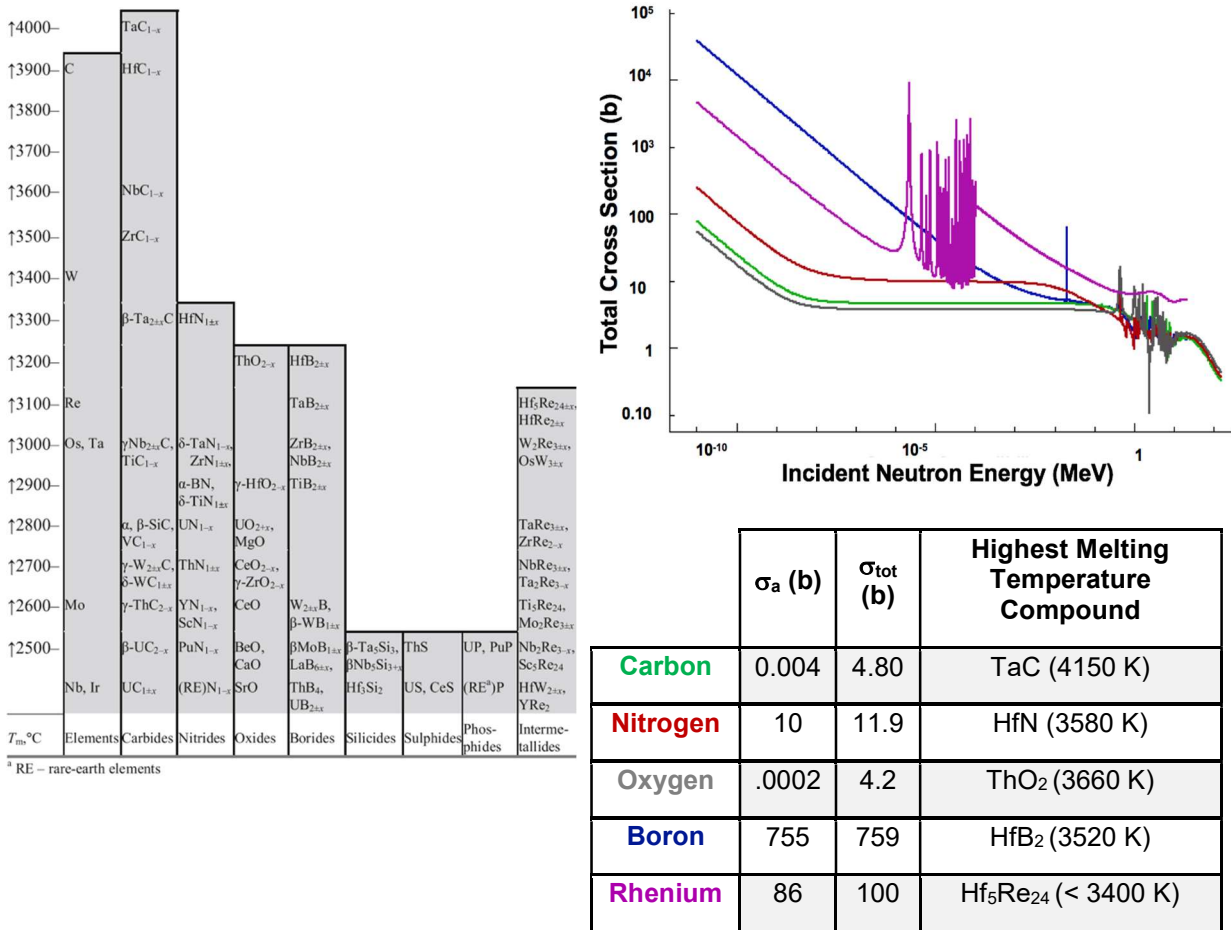


Figure A.1. Comparison of the neutronic properties of different ultra-high temperature compounds [45, 110]

Fundamental Considerations for Transition Metal Carbides to Support NTP

Transition metal carbides have the highest known melting temperatures for all known compounds and are chemically compatible with hydrogen. Because of this, refractory carbides are recognized to have the potential for highest NTP fuel operation temperatures (3000 – 3400K) and fuel endurance at temperature [1, 37, 38]. Refractory carbide materials, zirconium carbide (ZrC) and niobium carbide (NbC), were initially developed for the U.S. NTP program as coatings to protect graphite-based fuel systems of the Rover/NERVA program. Due to the recognized brittle nature of refractory carbides, there has not been a proposed engine design with a structural refractory carbide matrix, despite the potential for extremely high temperature operation. Instead, transition metal carbide fuel systems are typically proposed to form a solid solution with uranium carbide fuels to form extremely high melting temperature fuels that demonstrate thermal and chemical stability in the reducing hydrogen atmosphere [23, 40-42]. All-carbide solid-solution fuels (UC-ZrC, UC-NbC, UC-TaC, UC-ZrC-TaC, UC-NbC-TaC) were studied and tested extensively by the former soviet union [41-43] and underwent US development and testing via the Nuclear Furnace (NF-1) test late in the NERVA/Rover program [40]. The most significant progress in the development of these fuel systems were undertaken by the former soviet union, designed all-carbide solid-solution fuels did not function as structural matrices and latter fuel development aimed to manufacture geometries which could better withstand the power densities and corresponding thermal loadings of the NTR core [42, 111]. The major limitations of all-carbide fuels are their extreme brittleness and limited solubility with uranium carbide at elevated temperatures, which reduces total U-loading within the fuel [44, 112].

Recent advances in the production of fully ceramic microencapsulated (FCM) matrix fuels, have supported the viability of refractory carbide matrix candidates for light water reactor (LWR) fuel systems. Manufacture of discrete fuel particles embedded within a refractory carbide matrix, such as silicon carbide, of greater than 40 vol% has been demonstrated [113]. Further, recent development of carbide fiber reinforced ceramics, using melt infiltration techniques, has demonstrated the development of high density SiC, ZrC, HfC, and TaC composites which reduce typical processing time and exhibit superior high temperature operating performance than traditional manufacture of fiber reinforced composites [114]. Due to the poor thermal shock resistance of past all-carbide fuel forms, matrix fiber reinforcement may be necessary. In many performance applications, the use of fiber reinforced matrix composites has increased the use of high performance ceramics by enhancing the brittle material's resistance to thermal shock and increasing material durability. For example, originally studied for use in space shuttle turbopumps,

Herbell et. al. demonstrated fiber reinforced SiC composites could withstand the thermal shock from temperature gradients of up to 1900 K without significant degradation [115]. Modern manufacturing developments in melt infiltration techniques have demonstrated outstanding performance of carbon fiber reinforced carbide ceramic composites by allowing for higher achievable densities compared to higher purity chemical vapor infiltration (CVI) techniques [114]. Testing of ZrC-C_f composites has been completed in oxidizing chamber environments up to ~2673 K and shown outstanding high temperature performance and corrosion resistance compared to traditional techniques [116]. Still a knowledge gap remains for high temperature irradiation performance of carbide composites. Low and intermediate temperature irradiation testing has been completed on SiC FCM LWR fuels and SiC-SiC composite structures [55, 117]. In general, carbides such as SiC and ZrC show excellent resistance to irradiation effects and have been optimized to achieve good fiber stability at temperatures of interest to LWR applications. For reinforced SiC-SiC composites tested at temperatures between 1073 – 1573 K (800 - 1300°C), no significant decreases in fiber strength decrease for doses up to ~6 dpa were exhibited [117]. However, at higher operating temperature regimes (>1200°C), the onset of non-saturable void swelling is expected in SiC [118]. Swelling of fuels may also be assisted via fission product production during operation. Swelling in NTP fuels affects fuel dimensional stability is expected to affect mechanical and thermal loading profiles. NTRs typically operate for low burnup and the impact of swelling on fuel integrity compared to other degradation mechanisms (thermal stresses, cyclic fatigue, creep, etc.) is currently unclear.

While refractory carbides appear to promise excellent performance and the ability to combine the best aspects of both cermet and graphite composite fuels: hot hydrogen compatibility, low natural thermal neutron absorption cross sections, and extremely high temperature operation, development status is the lowest out of all other potential material candidates. Known feasibility issues can be addressed through modern design techniques and manufacture technologies. However, due to low development status overall, potential performance limitations still remain unknown.

Discussion

The current development status and known performance limits of applicable high temperature materials have been discussed. Table A.1 summarizes this knowledge and presents thermal scattering and absorption cross sections of relevant isotopes to support LEU NTP structural matrix

Table A.1. Properties of Elements of interest for Structural Nuclear Thermal Propulsion Fuel Systems [45, 46].

Element	σ_s (b)	σ_a (b)	Natural Abundance (at%)	Melting Temperature (K)	Key Attributes	Limiting Feasibility Issues
Iridium ^{193}Ir	14 -	425 111	- 62.7	2719	Extremely Inert	- Low melting temperature - Highest thermal absorption cross section
Niobium	6.26	1.15	-	2740	Low DBTT	- Readily hydrides below 1073 K - Interacts with common U-containing compounds at high temperature
Molybdenum ^{92}Mo ^{94}Mo ^{98}Mo ^{100}Mo	5.71 6.00 5.81 5.44 5.69	2.48 0.019 0.015 0.127 0.4	- 14.6 9.1 24.3 9.7	2890	- Hot hydrogen compatibility - Low thermal absorption cross section	Vapor pressure limits to operating temperatures below 2470 K
Tantalum	6.01	18.3	-	3270	- Low DBTT - High operating temperature potential	- Readily hydrides below 1073 K - Interacts with common UC, UN at high temperature - High thermal absorption cross section
Rhenium	11.5	89.7	-	3438	- No DBTT - High operating temperature potential - Hot hydrogen compatibility	High Absorption Cross Section
Tungsten ^{182}W ^{183}W ^{184}W	4.60 6.10 5.7 7.03	18.3 20.7 10.1 1.7	- 26.50 14.31 30.64	3695	- Hot hydrogen compatibility - High operating temperature potential - High uranium fuel loading	- High DBTT - High thermal absorption cross section
Graphite	5.55	0.0035	-	4000 ¹	- High operating temperature potential - Manufacturability - Lowest absorption cross section	- Chemically incompatible with hot hydrogen - Poor mechanical properties in tension
Carbides SiC ² WC ² TiC ZrC NbC HfC TaC	 7.25 10.15 9.90 12.01 11.81 15.79 11.56	 0.16 18.30 6.09 0.19 1.15 104.1 20.60	-	 3000 ¹ 3140 3430 3910 3770 4250 4250	- Highest operating temperature potential - Low absorption cross section - Good hot hydrogen compatibility	- Highest DBTT - Poor thermal shock resistance - Lowest development status

¹Sublimation temperature in vacuum temperatures

²Anticipated poor hot hydrogen propellant compatibility for high operating

concepts. Tungsten, graphite, and refractory carbide-based fuels are most applicable for LEU NTR applications.

Graphite offers the highest moderating power, (figure 2) extremely high operating temperature potential, and the largest database of operational experience. However, the major drawbacks of graphite based fuel systems are their incompatibility with the hydrogen propellant and poorer tensile properties, which requires significant design and development to avoid loss of structural support and hot hydrogen corrosion. Originally developed in parallel to the NERVA/Rover graphite fuel systems, W-cermet fuel systems addressed the limiting properties of the graphite matrix by allowing for superior high temperature strength and endurance, as well as compatibility with the hydrogen propellant. Unfortunately, the large absorption cross section of natural W requires isotopic enrichment to W-184 and high volume loadings of UO_2 or UN fuel. UO_2 and UN are thermodynamically unstable at temperatures necessary for NTR operation and require significant development and design to retain fuel within the W-matrix, which is desired in order to maintain reactor neutronics and fuel structural integrity. Refractory carbides were the last fuel system investigated in the United States and were the attention of significant development in the Russian NTP program [42, 43]. Refractory carbides offer the highest melting temperatures, high temperature thermal stability, and have low corresponding absorption cross sections. The low vaporization rates of refractory carbides at high temperature (figure A.2) can enable longer fuel lifetimes and increased fuel endurance compared to reference fuel systems. Refractory carbides may be better suited as a structural matrix rather than restricted to UC containing compounds. High moderating power and capability for increased uranium loadings of refractory carbide matrix fuels, compared to traditionally developed fuels, can allow for small engine size geometries desired for the LEU NTR without isotopic enrichment of the matrix.

Due to the efforts of historic NTP fuel development programs, design solutions have been postulated and determined for the known failure modes of each system. However, no fuel system has yet reached the development status to be flight ready. Implementation of new manufacturing techniques and design strategies should be realized prior to fuel qualification in order to reduce overall development cost. All in all, each fuel system will need to undergo rigorous testing to build a reliability database prior to approval for use in a mission.

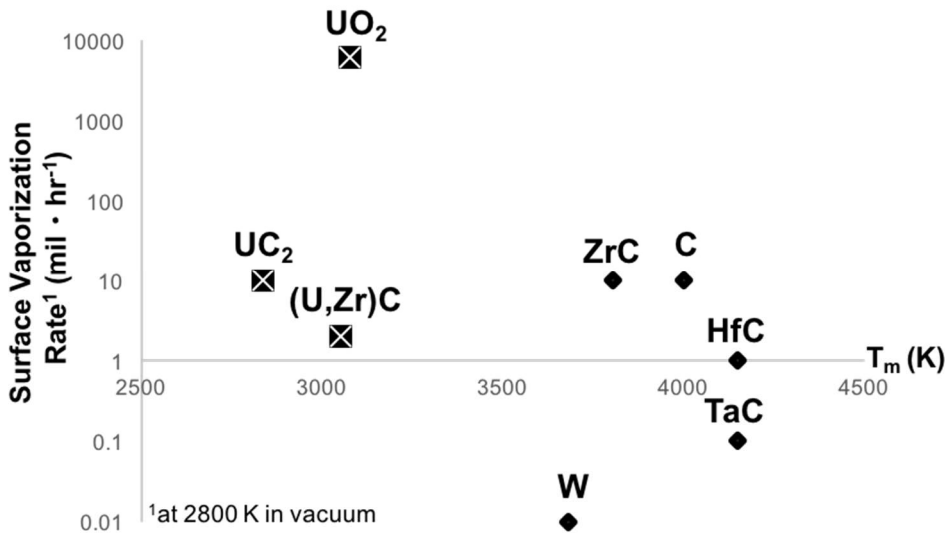
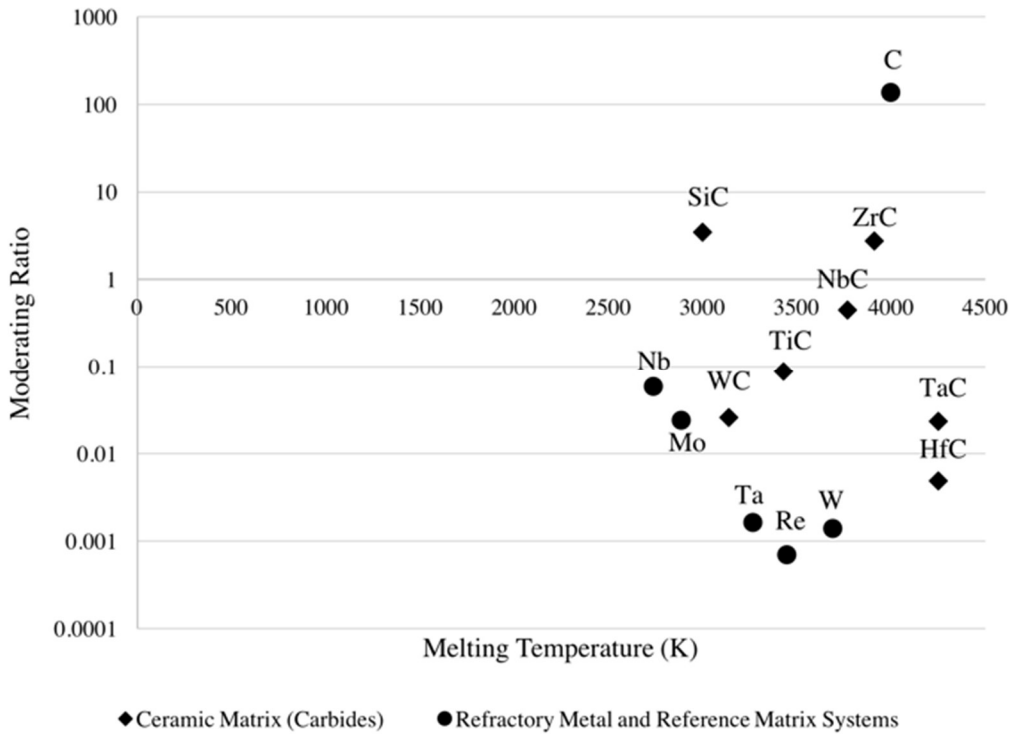


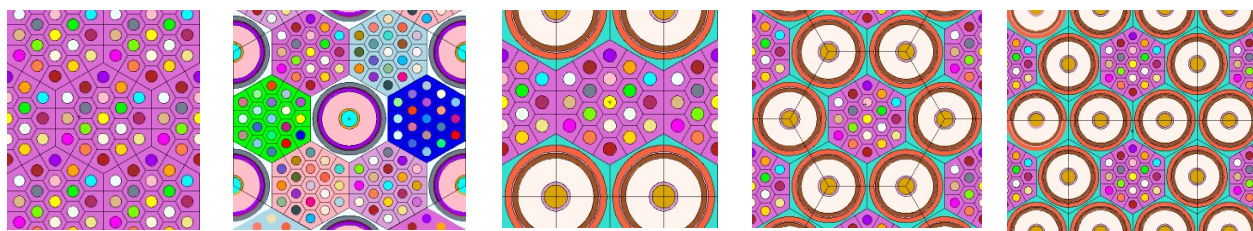
Figure A.2. Top. Calculated moderating ratios of graphite, transition metal, and refractory carbide candidates [45, 46]. **Bottom.** Surface vaporization limits total fuel operational lifetime. Surface vaporization rates are displayed for nuclear thermal propulsion material candidates replotted from [24].

Comparison of Matrix Concepts: Infinite Lattice Calculations

As a baseline, to initially evaluate the performance potential of each fuel system for use in a LEU NTR, infinite lattice calculations were performed and the infinite lattice multiplication constant (k_{inf}) derived for each fuel type. The infinite lattice calculations were completed using MCNP6 v1.1 with the ENDF/B-VII.1 neutron library. Each calculation used 360,000 particles per cycle with 7,232 active and 42 inactive cycles. The standard deviation associated with the calculated k_{inf} values are all below 0.00025, providing sufficient confidence in the statistical validity of the results. Graphite, tungsten, and refractory carbide based fuel systems were modelled as structural matrix type fuel elements. In each case, fuel elements were modelled using an extruded hexagonal geometry with 19 axial coolant channels based upon a reference NERVA geometry. Hexagonal fuel elements were simulated with a flat-to-flat distance of 1.905 cm (0.75 in.) and constant coolant channel radii of 0.1125 cm (0.045 in.). Reflecting boundary conditions were applied to all six sides to simulate an infinite lattice.

Graphite and tungsten matrix fuel systems were based upon reference composite (graphite) and cermet (tungsten) fuel systems proposed for small thrust LEU engine designs. The reference graphite composite matrix was modelled based upon a derivative of the NERVA/Rover Small Nuclear Reactor Engine (SNRE) design requirements with 19.75 wt% ^{235}U enrichment of the fuel. The graphite composite is composed of a 35 vol% (U,Zr)C fuel web dispersed within a graphite structural matrix with a 15vol% void fraction to accommodate fission product damage. Total uranium loading of the graphite composite matrix fuel is limited to 0.64 g/ccm. Reference tungsten matrix fuels are based upon the enriched LEU-cermet fuels for the Space Capable Cryogenic Thermal Engine (SCCTE) reference core. The cermet fuel is modelled using 60% volume loading of UO_2 with 6 molar % ThO_2 and a W structural matrix composed of 95 w/o enriched W-184. Refractory carbides were modelled as structural matrix fuel forms based upon FCM fuel design. The proposed refractory carbide matrix fuels are modeled as a homogenized material with 35 vol% UO_2 loading (fuel coatings neglected) with 19.75 w/o U-235 enrichment. Refractory carbides with high moderating power were surveyed: SiC, ZrC, and TiC. In all fuel element designs, matrix material was modelled as homogenized.

Each fuel type was studied with and without external moderating elements. To determine the effect of moderation on fuel reactivity, fuels were arranged in 1:1, 1:2, 1:3, and 2:1 moderator ratios with reference $\text{ZrH}_{1.8}$ containing moderator tie-tube elements optimized in previous studies [13, 119]. Figure A.3 shows the infinite lattice configurations for the 1:0, 1:1, 1:2, 1:3, and 2:1 fuel to moderator (F:M) ratios. The calculations were completed using room temperature cross-



No Moderator

2:1 F:M Ratio

1:1 F:M Ratio

1:2 F:M Ratio

1:3 F:M Ratio

Figure A.3. Schematic of the infinite lattice configurations with moderator elements for LEU fuel analyses.

sections for the tie-tube moderator elements, while an average temperature of 1600 K was assumed for cross sections for the fuel matrix material and the UO_2 s(a,b) card.

Refractory carbide matrix fuels exhibited superior k_{inf} values to the reference designs of SULEU cermet fuels and SNRE composite fuels (figure A.4). Enriched tungsten cermet fuels performed the poorest with regard to calculated k_{inf} values, needing significant moderation (F:M ratio > 1:1) to achieve criticality. Refractory carbide and graphite matrix candidates have lower absorption cross sections and atomic masses and are thus capable of greater moderation than the best W-isotopes. Although the graphite matrix has the highest moderating power of all of the presented high temperature materials (figure A.2), reduced fuel loadings, necessary to maintain fuel mechanical integrity and produce the high melting temperature (U,Zr)C fuel web, of this fuel system type do not allow for initial criticality using LEU in NERVA-derivative geometries without external moderating elements.

Because of the potential of refractory carbides to be discretely loaded with particles of uranium containing compounds (such as UN, UC, UO_2 , etc.), higher overall U loading and moderating powers may be achieved. This allows for the criticality of these fuels to be achieved without use of an external moderating element. Best k_{inf} performance is achieved with the use of a SiC matrix. However, SiC does not have the potential for as high operating temperatures as other refractory carbide matrix candidates and has reduced hydrogen compatibilities. ZrC and TiC fuels also have the potential unmoderated LEU engine designs. Moderated ZrC matrix fuel systems behave similarly to moderated graphite composite fuels and have potential for much higher operating temperatures in the hot hydrogen environment.

Conclusions

Ultra-high temperature materials to enable nuclear thermal propulsion and LEU engine designs do exist, at varying levels of development status. Material candidates with greatest potential for LEU NTP: graphite, tungsten, and refractory carbides, offer the potential for the highest operating temperatures, compatibility with the hydrogen propellant, uranium compounds and protective claddings, and have undergone a degree of development specific to NTP applications. It has been demonstrated in previous studies that reference graphite and tungsten fuel systems developed during previous fuel programs can be used in a LEU engine with the assistance of isotopic enrichment or external moderating elements. In this study, manufacturing limits and design techniques identified through historic and modern programs have been identified and are shown enable critical infinite lattice geometries using derived NTP fuel form geometries. Notably,

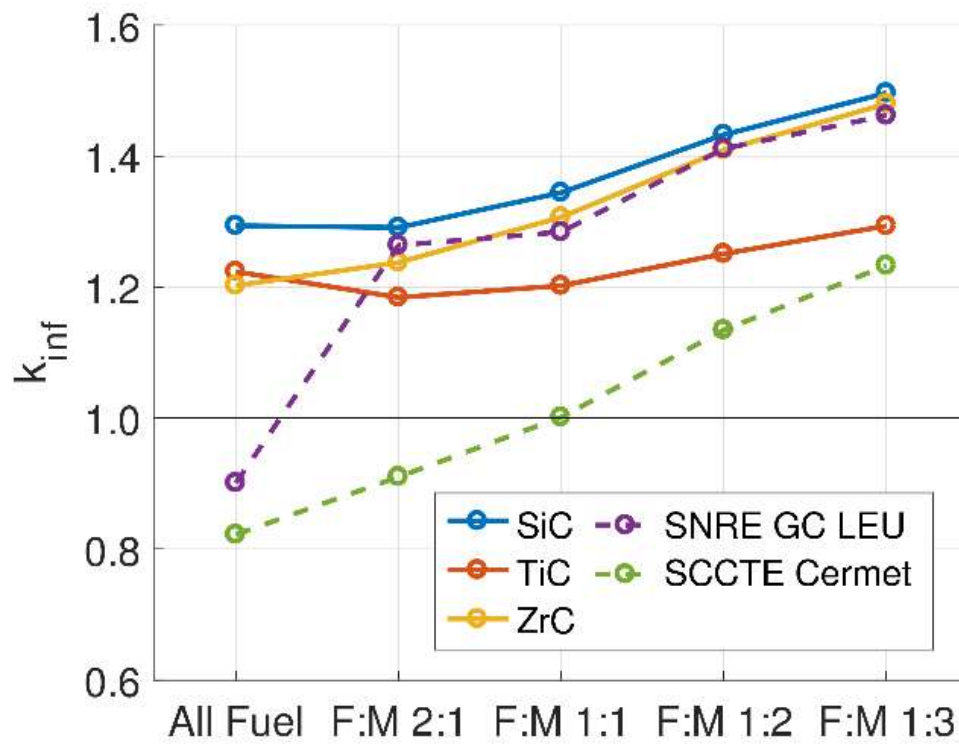


Figure A.4. Calculated k_{inf} of selected nuclear thermal propulsion fuel systems.

refractory carbide fuel systems can allow for critical LEU engine designs without enrichment or external moderating elements, but correspond to the lowest level of fuel development status.

Ultimately, it should be kept in mind that the refinement of fuel design and specifications of the NERVA/Rover and GE-710 reactor programs was due to accumulated operational experience and reaction to experimental test data. For example, original NERVA/Rover graphite matrix fuels utilized discrete fuel particles dispersed within the graphite matrix, but later shifted design to the lower U density (U,Zr)C fuel web in order to reduce the buildup of thermal stresses between fuel particles and the graphite matrix which lead to intra-matrix cracking and fuel failure. This performance data is extremely valuable to accelerate initial future development/optimization efforts of derived LEU type engines and fuels.

However, no fuel system has yet reached the development status to be flight ready. Each fuel system will need to undergo rigorous testing to build a reliability database prior to approval for use in a mission. Program and mission requirements will ultimately drive the prioritization of desirable material properties and fuel development status. Maturation of new fuel systems and corresponding manufacturing techniques compliments the current development path by reducing risk associated with previously developed fuels and offering opportunities for breakthrough technologies that could enable new missions or capabilities.

The presented study compares un-optimized refractory carbide matrix fuels to reference LEU reactor fuel systems only in order to qualify refractory carbide matrix performance. In order to verify the applicability of refractory carbide matrix fuels, initial experimental and analytical studies should aim to quantify acceptable fuel loadings, necessary fuel coatings, impact of thermal stresses, chemical stability at the matrix-particle or matrix-fiber interfaces, thermodynamic stability of the matrix under high temperature irradiation in a hot hydrogen environment, as well as capture limiting operating regimes. More detailed fuel studies to optimize fuel geometry and engine sizing are suggested to better qualify the performance of a loaded refractory carbide fuel systems in NTP systems and quantify the impact of intrinsic moderation of the fuel matrix on meeting engine performance and operating requirements.

Acknowledgments

Kelsa Benensky is sponsored by a NASA Space Technology Research Fellowship.

Appendix B. RC-FCM Design Description and Analysis for LEU NTP Applications

(from K. Benensky et. al. Nuclear and Emerging Technologies for Space Conference 2018)

Originally developed to enable very high burnups and enhanced accident tolerant fuels for terrestrial power reactors, fully ceramic microencapsulated (FCM™) fuels offer a modern alternative fuel system design for nuclear space applications. Composed of a structural refractory carbide (RC) matrix (SiC, TiC, ZrC, etc.) impregnated with coated uranium compound particles (UO₂, UN, etc.), RC-FCM is a derivative of the original NERVA/Rover loaded graphite matrix fuels. Most refractory carbides are compatible with the hydrogen propellant and are some of the highest known melting temperature compounds, which may enable enhanced tolerance to desirable nuclear thermal propulsion (NTP) operating conditions. This paper summarizes the combined experimental and modelling efforts recently undertaken to survey FCM fuel for NTP applications. Sensitivity of fuel system design to fuel volume loading (UO₂ and UN) with low enriched uranium (< 20 at% U-235) on fuel reactivity was surveyed through infinite lattice calculations using monte carlo n-particle (MCNP) reactor physics code.

Introduction

Nuclear thermal propulsion (NTP) is an in-space propulsion technology capable of high specific impulse (850 – 950 s) and thrust levels (10 – 250 klbf). In a nuclear thermal rocket (NTR), the heat from nuclear fission is transferred from the fuel to directly heat a propellant, which is expanded out a nozzle to provide thrust. When optimizing for high Δv , these desirable performance parameters allow for reduced crewed interplanetary trip times to minimize the crew's exposure to harmful physical and psychological health effects from microgravity, space radiation, and prolonged confinement during transit. To enable the high performance of NTP engines, current designs call for a corrosive hydrogen (H₂) propellant heated to engine outlet temperatures between 2500 – 3000 K. While NTRs operate at extremely high temperatures compared to terrestrial power reactor designs, NTRs require very low fuel burnups and short operating lifetimes. For crewed Mars missions, NASA's 2015 in-space propulsion technology roadmap calls for 85 – 102 minutes of operation at full power, composed of four burns (maximum burn time of 46 minutes) [15]. The identification of a robust fuel form capable of predictable performance over the range of operating conditions of the NTR is critical to the successful development of NTP systems.

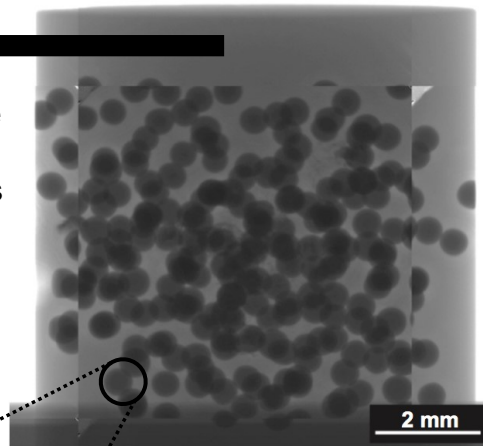
Refractory Carbide Fully Ceramic Microencapsulated Fuel Systems

At the minimum, NTP fuel system design should enable the operating temperatures in excess of 2500 K, compatibility with the H₂ propellant, and have good nuclear properties to enable criticality. Other desirable design attributes would include a robust fuel with protective coatings which can survive thermal shock and thermal cycling, as well as to prevent hydrogen attack of the fissile fuel or prevent fissile fuel migration and escape from a structural matrix. An ideal fuel form should also limit the escape of fission products and irradiation damage to the fuel matrix to ease handling of tested fuels and prevent undesirable microstructural changes caused by irradiation effects. Refractory carbide fully ceramic microencapsulated (RC-FCM) fuel systems offer a variety of design features which may offer enhanced tolerance to NTP operating conditions compared to legacy fuels from historic NTP development programs. Originally developed to withstand high operating temperatures and burnups for Gen III+, Gen IV power reactors, RC-FCM fuel systems are composed of a refractory carbide structural matrix with dispersed coated fuel kernels (figure B.1). Current FCMTM technology employs a monolithic silicon carbide (SiC) matrix with dispersed tri-structural isotropic (TRISO) fuel particles [59]. SiC is known to volatilize in hot H₂ (reaction to form gaseous corrosion products), similar to graphite-based fuel systems, which would limit operating lifetime at high temperatures ($T > 1700$ K). Other refractory transition metal carbide candidates such as zirconium carbide (ZrC), titanium carbide (TiC), niobium carbide (NbC), etc. do offer H₂ compatibility over the temperature range expected during operation and are traditionally used as protective coatings on graphite/carbon elements in high temperature oxidizing and reducing environments, as well as vacuum furnace applications to extend lifetime at ultra-high temperatures due to their low vaporization rates [112]. These materials correspond to some of the highest known melting temperature compounds and have the potential to enable ultra-high temperature operation above 3000 K, similar to tungsten (W) matrix ceramic-metallic (cermet) fuels. Use of discrete, dispersed, coated fuel particles has the potential to enable higher fissile fuel loadings compared to composite fuel systems, as well as offer a variety of other protective features via multiple fuel coatings:

- *Structural refractory carbide pressure vessel coating prevents fuel migration and vaporization at high temperature and retains fission products (FPs)*
- *Multiple coatings are additional barriers to H₂ penetration and attack of fissile fuel kernels, as well as offer FP attenuation prevent FP interaction with the matrix or localized matrix damage via FP recoils*

Structural Refractory Carbide Matrix

- Allows for ultra high temperature operation (2350 – 3200 K)
- SiC, ZrC, TiC, and NbC matrices allow for LEU compatibility without isotopic enrichment or external moderating elements
- Offers hydrogen compatibility to protect fuel particles from hydrogen attack



Advanced TRISO

- Fuel Kernel: UO_2 , UN, UC_2 , etc.
- Multiple barriers of protection retain fissile fuel kernel for ultra high temperature operation (> 3000 K)
- Attenuates fission products to reduce irradiation damage of the matrix
- Refractory carbide pressure vessel layer traps fission products to prevent escape into propellant or interaction with the matrix

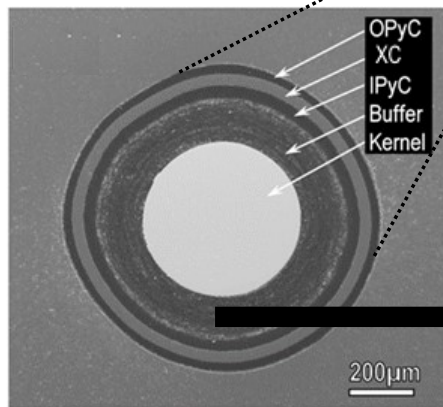


Figure B.1. Design description of the proposed RC-FCM fuel system. Figures adapted from [59].

Refractory carbides offer low thermal neutron absorption cross section and good moderating power to allow for flexibility in designing high or low enriched uranium (HEU or LEU) systems, which do not require enrichment of matrix materials or use of external moderating elements (NF-1 type tie-tubes). Modern manufacturing techniques, such as spark plasma sintering (SPS) can allow for the production high melting temperature composite materials with more desirable microstructures than historically available methods. Production studies from on-going accident tolerant fuels research, have demonstrated TRISO particle loadings of greater than 40 vol% in SiC [113].

MCNP Analysis

In order to understand the impact of fuel volume loading and matrix composition on potential fuel reactivity, infinite lattice calculations were performed using Monte Carlo N Particle (MCNP 6.1.1beta) reactor physics code [120]. Fuels were modelled in an infinite lattice using the legacy NERVA/Rover hexagonal fuel element geometry: 0.75 in. (1.905 cm) flat-to-flat with 19 x 0.045 in. (0.01125 cm) axial diameter coolant channels. To meet LEU requirements, uranium enrichment was limited to 19.75 at% U-235. No external moderator elements were included in the infinite lattice calculations. Reflective boundary conditions were utilized at each of the six fuel faces to simulate the infinite lattice. Each calculation used 36,000 particles per cycle with 72 active and 40 inactive cycles. The calculations were completed using homogenized fuel compositions with 1600 K cross sections for the homogenized fuel and the UO₂ s(a,b) card. Two cases were surveyed through infinite lattice calculations:

1. **Ceramic-ceramic (cercer):** dispersed uncoated ceramic fuel particles in a structural refractory carbide (ceramic) fuel matrix similar to conventional structural matrix NTP fuel designs from the historic NERVA/Rover and GE-710 programs of the United States.
2. **RC-FCM:** dispersed coated fuel particles in a structural refractory carbide matrix. The coated particle design consists of a central fissile fuel kernel, surrounded in a porous carbon buffer layer, which is contained with an external refractory carbide pressure vessel coating. Kernel particle diameters were modelled as 250 μm with a 50 μm thick carbon layer (figure 2).

Cercer fuel volume loadings of: 5, 10, 15, 20, 25, 30, and 35 volume % (vol%) uncoated UO₂ and UN particles in SiC, TiC, and ZrC matrices were modelled in MCNP (figure B.3). Additional modelling was completed for FCM fuel volume loadings of: 10, 15, 20, 25, 30, and 35 vol% coated UO₂ and UN particles (figure B.2) in SiC, TiC, and ZrC matrices (figure B.4). Use of coated fuel

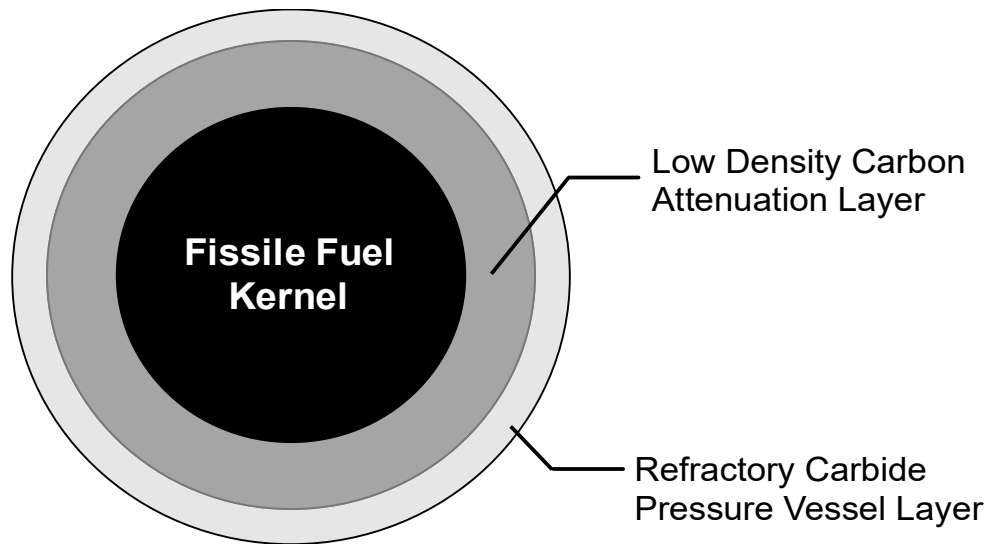


Figure B.2. Basic coated fuel particle geometry analyzed in this study. Fuel kernel diameter was modelled as 250 μm after sizes targeted in the Space Nuclear Thermal Propulsion (SNTTP) program [121]. Carbon coating thickness was modelled as 50 μm , which was the thickness used to coat fuel particles in the NERVA/Rover program [1].

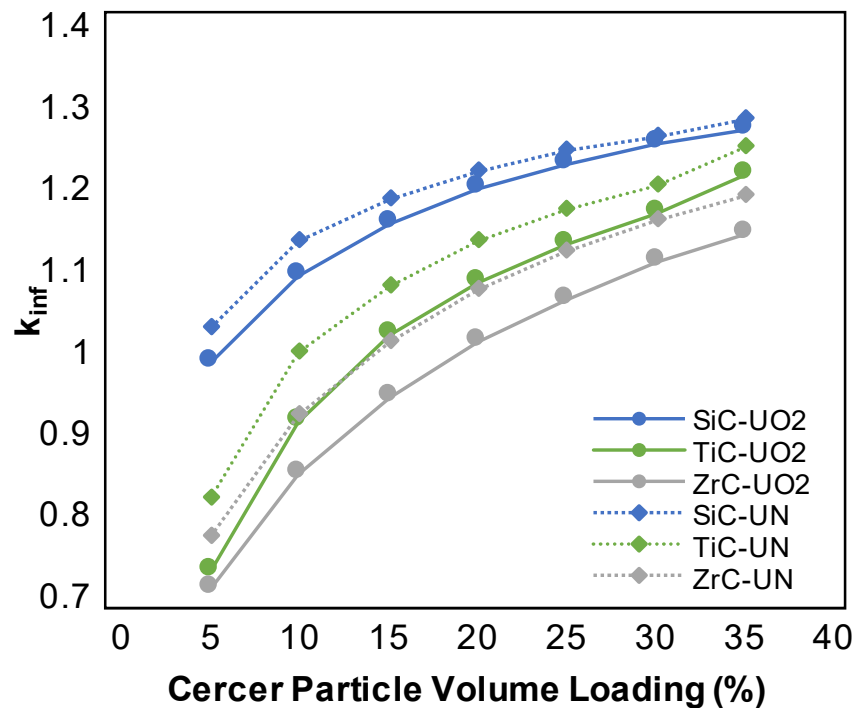


Figure B.3. Impact of UO_2 and UN volume loading on k_{inf} values of SiC, TiC, and ZrC matrix cermers.

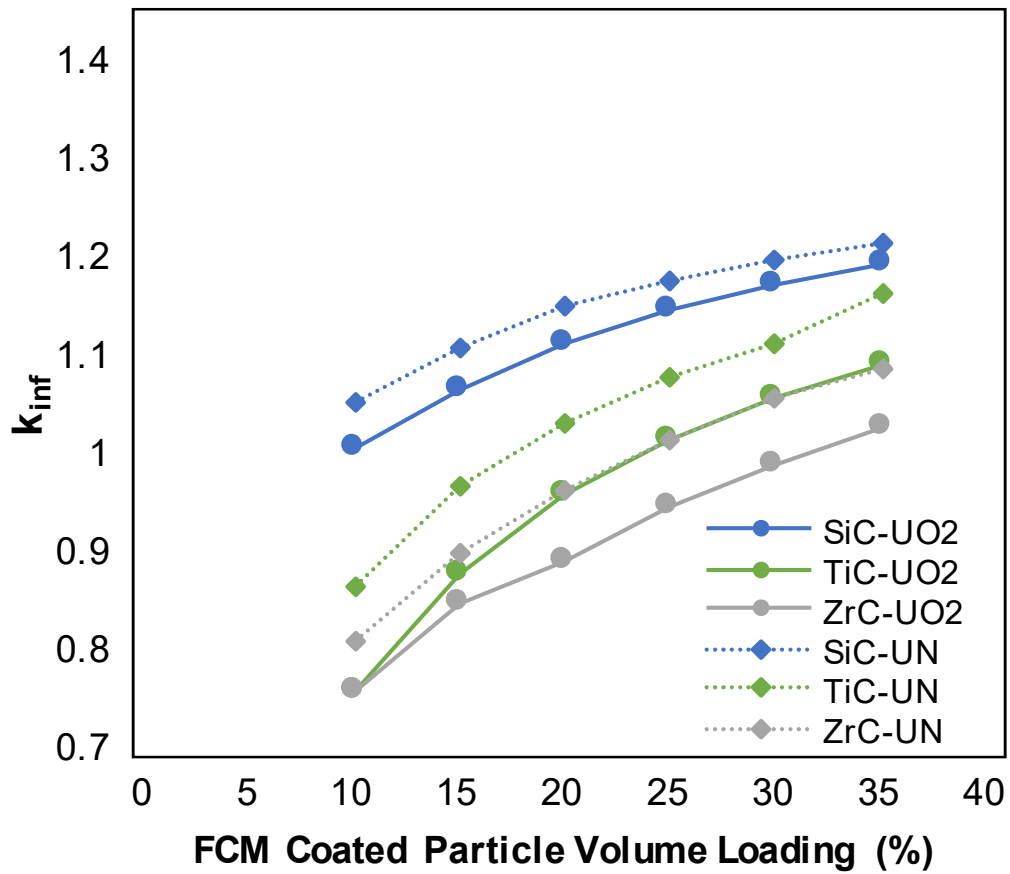


Figure B.4. Impact of coated UO₂ and UN volume loading on k_{inf} values of SiC, TiC, and ZrC matrix FCM fuels with 250 μ m diameter fuel kernels coated with 50 μ m low density carbon.

particles, reduces uranium loading by nearly a factor of two due to the volume allocated to coatings. This results in reduced calculated k_{inf} values for FCM type fuels compared to cermet fuel systems.

SiC matrix fuel systems exhibit k_{inf} values of greater than 1.0 for fuel volume loadings of greater than 10 vol%. TiC matrix fuels were calculated to have the second highest k_{inf} values for cermet and FCM fuel systems. TiC FCM fuel systems with monolithic $k_{inf} > 1$, no external moderating elements, are achievable with coated particle loadings of at least 25vol%. ZrC exhibited the lowest k_{inf} values of the LEU fuel systems presented and required at least 35 vol% coated UO_2 particle loadings for a $k_{inf} > 1$. However, previous studies have shown that inclusion of external moderating elements can increase the k_{inf} value of ZrC matrix cermet fuels compared to TiC [60].

Acknowledgements

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**Appendix C. Gibb's Free Energy Minimization Calculation Results for
SiC, TiC, and ZrC, to 10^{-8} mol**

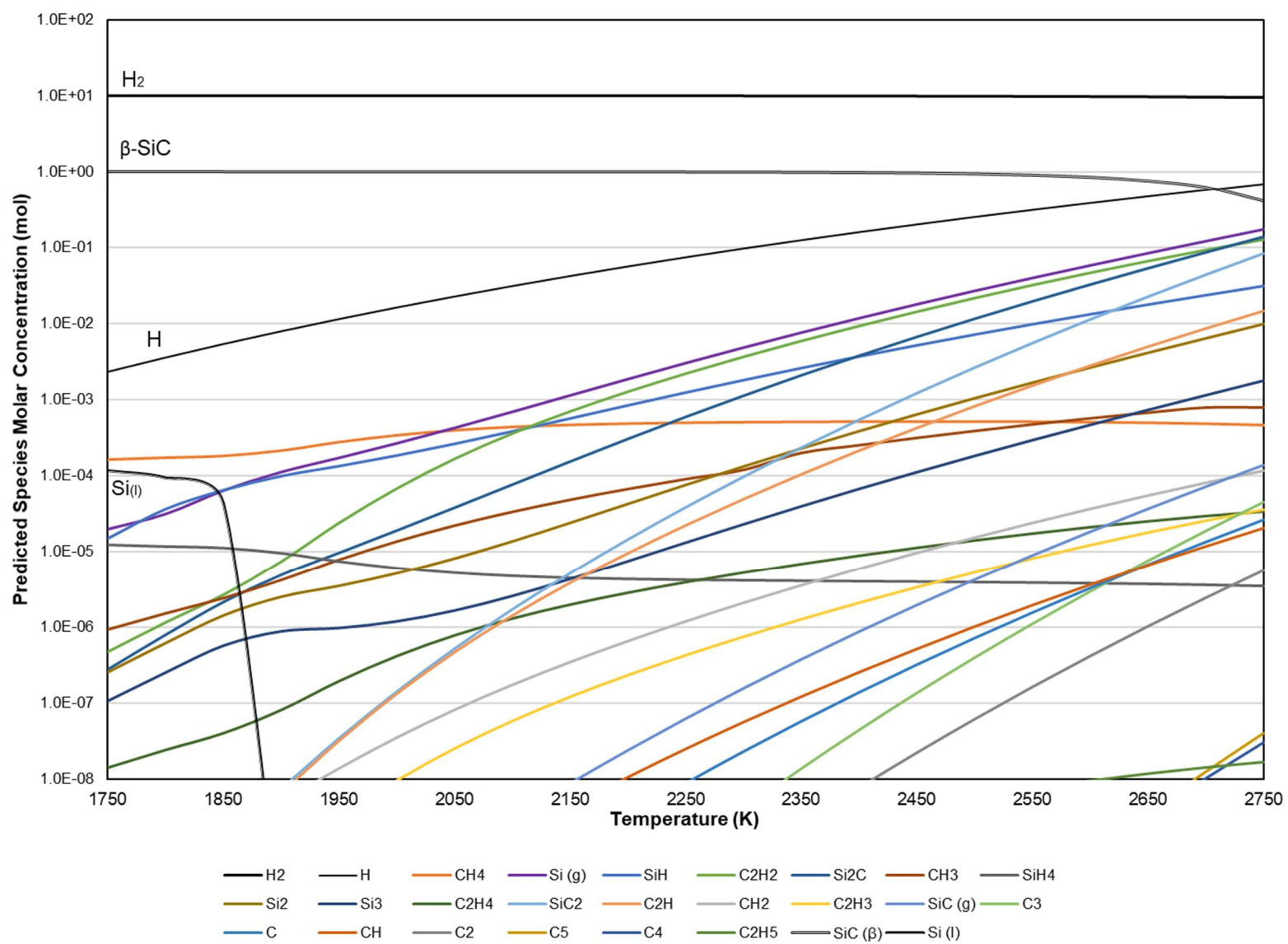


Figure C.1. Predicted corrosion products of the SiC- H_2 reaction at 1 atm pressure for temperatures of 1750 - 2750 K

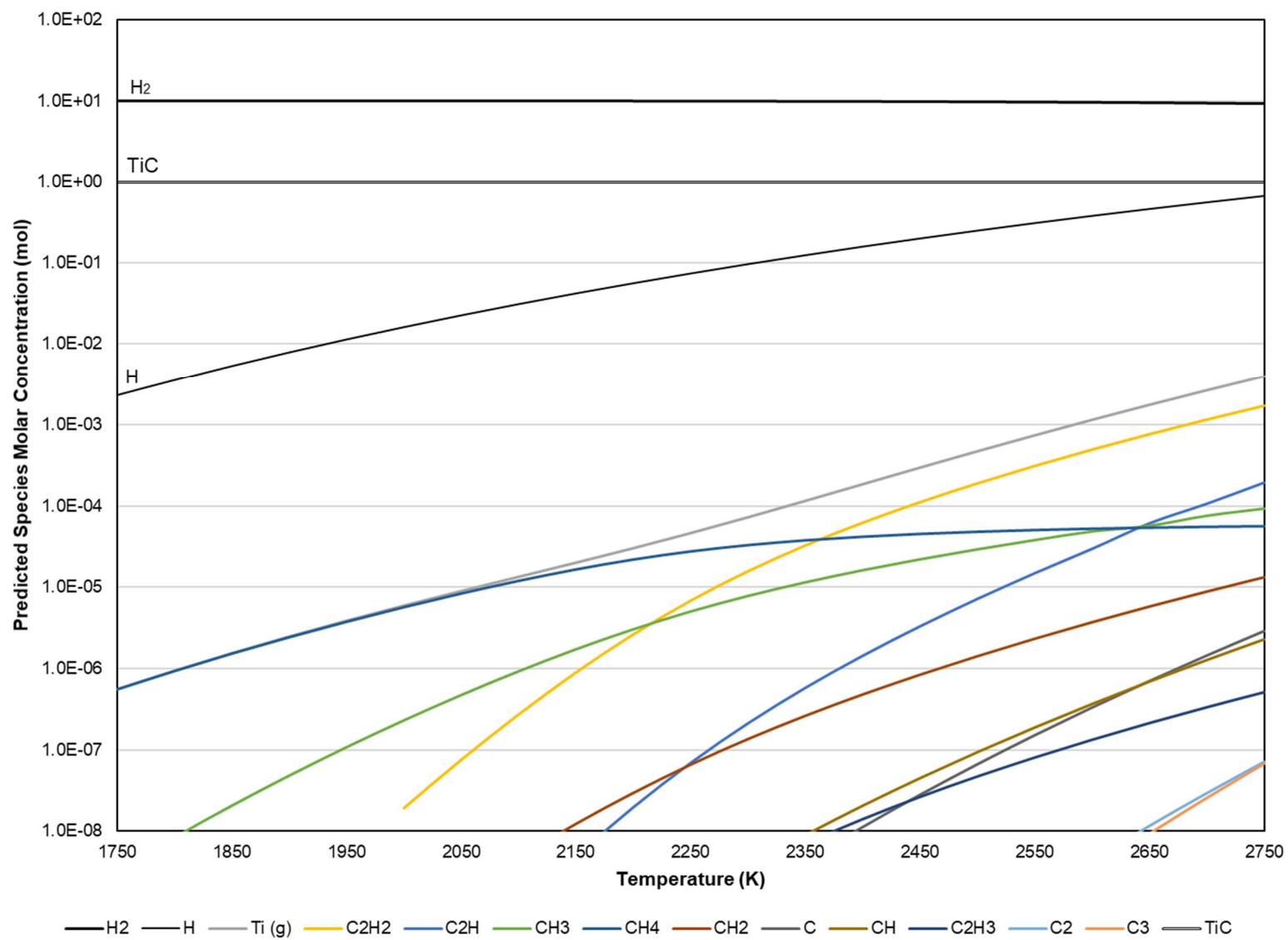


Figure C.2. Predicted corrosion products of the TiC-H₂ reaction at 1 atm pressure for temperatures of 1750 - 2750 K

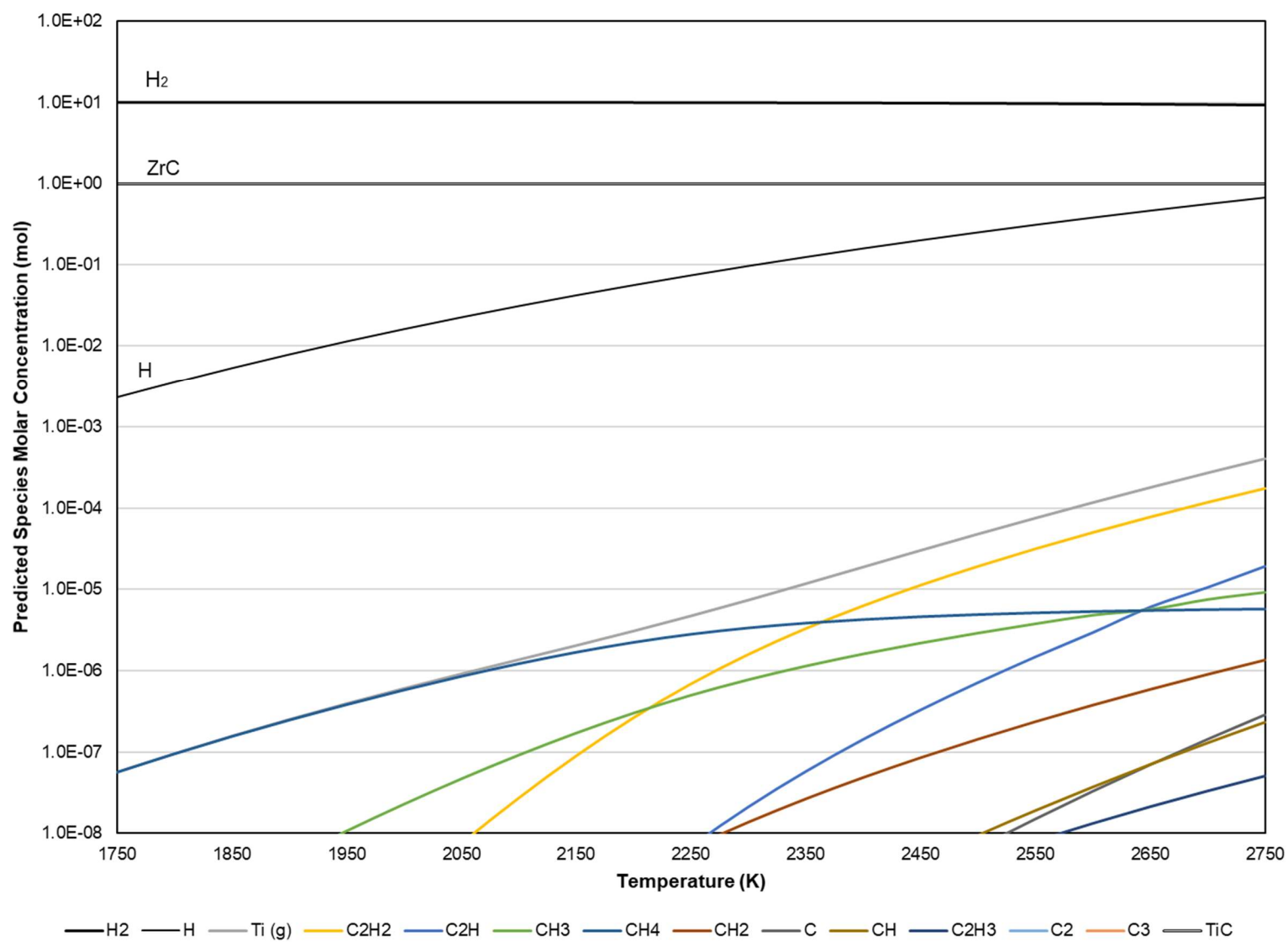


Figure C.3. Predicted corrosion products of the ZrC-H₂ reaction at 1 atm pressure for temperatures of 1750 - 2750 K

Appendix D. Operational Characterization and Testing of NASA MSFC's Compact Fuel Element Environmental Test (CFEET)

(from K. Benensky et. al. Nuclear and Emerging Technologies for Space Conference 2018)

Introduction and Upgrade Overview

Through the use of hydrogen propellant and operating temperatures in excess of 2000 °C, nuclear thermal propulsion (NTP) is a nonchemical propulsion technology capable of high specific impulse (800 – 1000 s) and thrust (100 – 1100 kN). Successful development of NTP technology must include maturation of fuel systems which are able to provide criticality to the engine, while retaining structural integrity during operation at extreme temperatures in the corrosive hydrogen environment. Subscale testing is a key element of the fuel development process. Subscale testing is intended to rapidly and affordably optimize the manufacture process parameters explored in the laboratory scale development phase to ensure the successful development of robust, full size fuel elements. The compact fuel element environmental test (CFEET) is an ambient pressure induction furnace capable of high temperature operation and hydrogen flow. The furnace is contained by a custom, water cooled chamber previously detailed in¹. CFEET has been used to test subscale surrogate and depleted uranium (dU) fueled nuclear thermal propulsion fuel samples. This paper details the design changes to the heating assembly and accompanying operational characterization recently undertaken to create more uniform sample temperatures and accurate test plans.

Induction Heating Considerations and Design

In order to rapidly heat samples to temperatures of 600 - 2900°C, CFEET utilizes induction heating. The ideal test apparatus should allow for uniform sample temperatures, flowing hydrogen, invariant holds at high temperature, and rapid/efficient heating of subscale fuel samples to understand their thermodynamic and chemical compatibility in a high temperature, reducing environment. To heat samples inductively, a high frequency, alternating current is passed through a water-cooled, helical, copper coil to create a magnetic field. The magnetic field interacts with an electrically conductive tungsten (W) susceptor producing eddy currents. Eddy currents resistively heat the susceptor to extremely high temperatures. The susceptor in turn heats the fuel sample which is placed coaxially inside the tungsten susceptor. The key advantage of induction

heating for NTP applications is the capability to quickly heat to (400 °C/min, 60 K/s demonstrated) and hold samples at ultra-high temperature for extended time periods.

Previously, the CFEET induction coil was directly coupled to subscale ceramic metallic (cermet) fuel coupons. The metallic fuel matrix allowed for the electrically conductive properties needed to generate an eddy current to heat the sample. However, without detailed analysis and coil customization, fuel sample thermal profiles have the potential to be non-uniform due to the shape of the magnetic field in proximity to the copper coil turns resulting in alternating high and low field strength regions. These regions result in variations in magnetic coupling within the fuel sample (figure D.1). Direct induction heating of samples also produces undesired, preferential heating at the sample outer diameter surface, known as the skin effect, in which most of the induction power generated to heat the sample is localized near the outer diameter, leaving the core of the sample at a cooler, and unobservable, temperature. An additional disadvantage of this approach is that it is limited to testing of metallic samples. Since induction heating requires electrical conductivity, ceramic materials with insulating or semiconducting properties would be poor candidates to heat in CFEET. Alternative NTP fuel concepts include ceramic materials: graphite, refractory carbide matrix composites, or all-carbides (consisting of uranium carbide in solid solution with transition metal carbides).

To avoid the required detailed design, verification testing, and analysis required to prepare CFEET for direct coupling and testing of materials with variant compositions and geometries with the current induction coil, a susceptor was introduced into the system setup. A susceptor is an electrically conductive workpiece which interacts with the induction coil in order to generate heat external to the sample. Heat is transferred to the samples via radiative or conductive heating. Since most of the heat generated via induction heating is concentrated on the outer diameter of a workpiece, typical susceptor geometries are usually a thin sleeve or tubing. Induction heating of a susceptor enables more uniform sample heating, heating of nonconductive materials, and repeatability of test conditions. Use of a susceptor has been demonstrated previously in various high temperature experiments undertaken to support historic nuclear space programs^{2,3,4}. Tungsten (W) was chosen as the desirable susceptor material due to its electrical conductivity, high melting temperature, compatibility with hot hydrogen, and low vaporization rate. These attributes enable the highest working temperatures and longest part lifetimes. In CFEET, the W susceptor allows for radiative heating of subscale samples centered within the heating assembly (figure D.2).

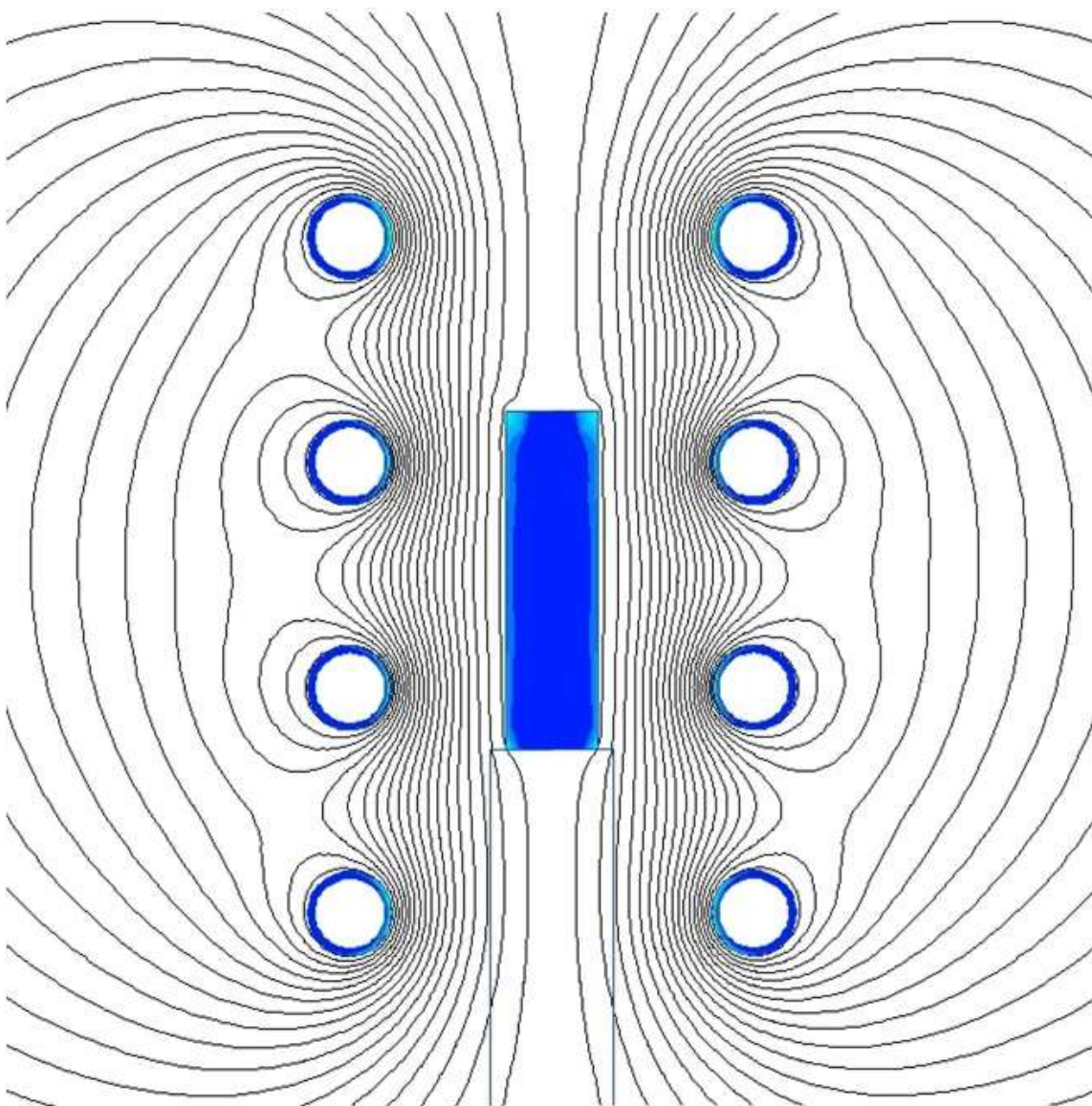


Figure D.1. Magnetic field profile variations. Note concentration of coupling at top and bottom edges of fuel sample at center.

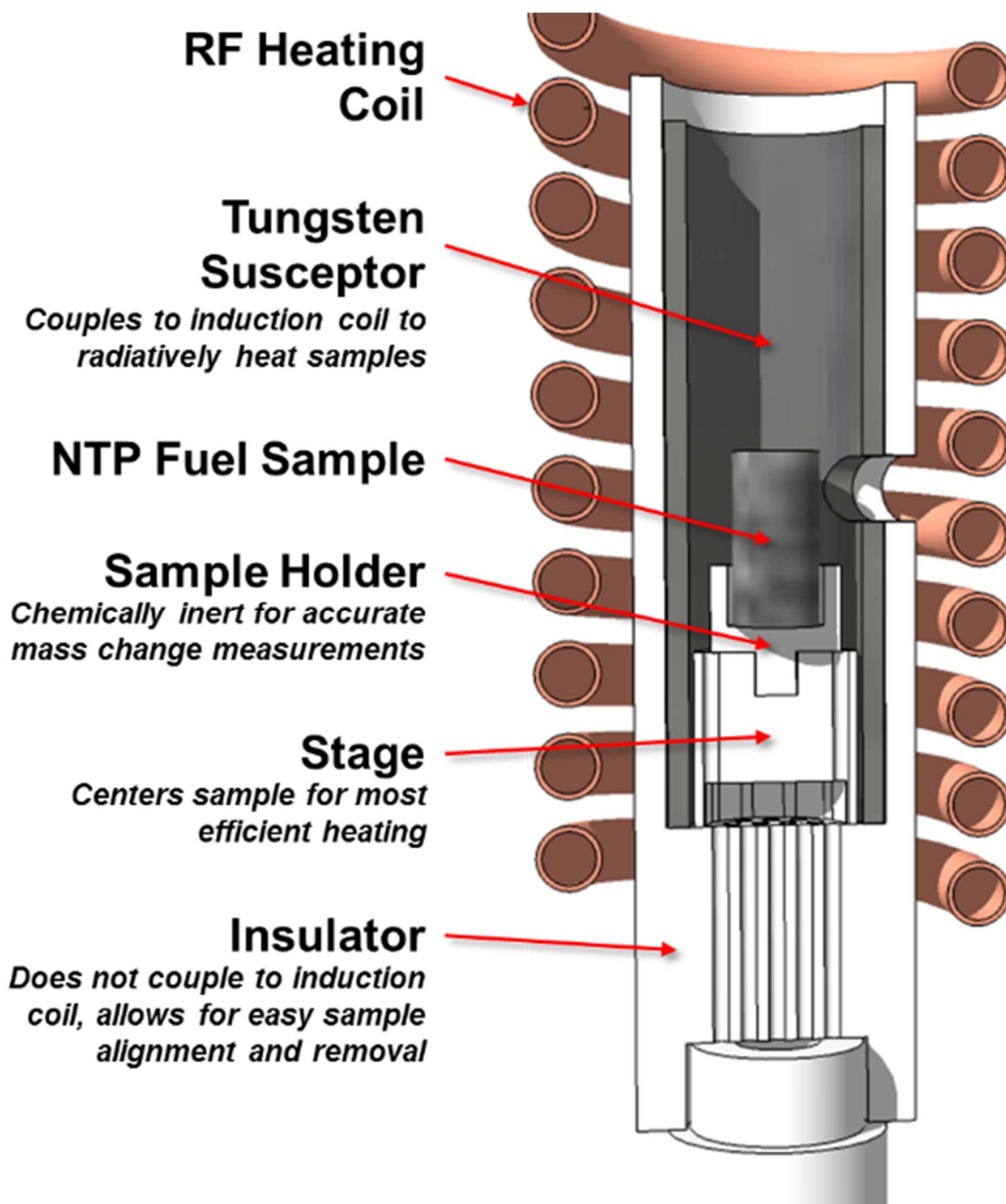


Figure D.2. Updated CFEET sample holder/heating assembly. A boron nitride (BN) insulator is used to contain the sample holder, stage, and W susceptor in a discrete assembly for easy loading and alignment of samples in the chamber.

Changes to Chamber Configuration and Upgraded Monitoring Equipment

The CFEET chamber has also been modified to allow for easier sample loading and alignment. Previously, samples were loaded from the bottom of the chamber using a feedthrough metal sealed vacuum flange with the sample holder stacked on top of boron nitride tubing (figure D.3).

This required samples be loaded into the chamber without visual sighting or manipulation to ensure the assembly is centered in the coil correctly and viewports properly aligned. Therefore, top loading was desired to allow for the fastest loading times, as well as easy inspection and alignment of the sample holder assembly once it is placed in the chamber.

The top of the chamber was modified to include a fast entry vacuum door. Quartz is chosen as the sight glass material for the vacuum fast entry door to allow for temperature measurement using an Ircon Modline® 5R two-color pyrometer (1.0 – 1.1 μm wavelength), as well as enable in-test video monitoring using an IP camera. Quartz is also compatible with the relatively high working temperatures ($\sim 200\text{ }^{\circ}\text{C}$), due to radiative heating losses from the sample holder assembly, required of chamber components during testing. Sample alignment is further assisted by addition of alignment plates at the base of the chamber to ensure the sample holder assembly is repeatedly placed centralized in the coil and can be quickly realigned in the case of new coil installation.

Power Supply and Coil Optimization

A custom copper induction coil was designed and manufactured at NASA MSFC to pair with the tungsten susceptor and sample holder assembly. Coil dimensions and specifications are displayed in figure D.4. The goal of the power supply and coil optimization was to ensure the operating frequency of the power supply was within rated limits (40 kHz optimum) and demonstrate repeatable susceptor and sample temperatures could be achieved with input power.

As discussed previously, the efficiency of heating is dependent upon coil and workpiece geometry. The Inductoheat Statipower® SP-16 50 kW, 50 kHz power supply was optimized for the susceptor-coil pair. A capacitance of 11.97 μF and transformer ratio of 30:1 was required in order to operate the power supply at 45 – 50 kHz. It was found that susceptor temperature is repeatable with input power, which helps to ensure that tests are repeatable among various samples or under thermal cycling conditions. Sample size, emissivity, and geometry were determined to play a secondary role in controlling the efficiency of heating available from the



Figure D.3. Original CFEET chamber design required loading from the bottom of the chamber. This configuration resulted in difficult sample alignment with relevant pyrometers and the induction coil since the sample holder assembly could not be manually manipulated once loaded into the chamber.



Coil Diameter: 2.39 in.

Tubing Diameter: 0.35 in.

Coil Pitch: 0.63 in.

Number of Turns: 8

Figure D.4 The copper coil geometry and power supply configuration were optimized for 50 kHz operation to allow CFEET to reach the temperatures of interest to NTP with the 50 kW power supply.

tungsten susceptor. Modelling efforts are underway to understand the impact of each of these parameters relevant to subscale fuel testing.

Pyrometer Characterization

Once it was demonstrated that susceptor temperatures were repeatable and the power supply configuration allowed for temperatures of interest to be achieved, it was desired to verify the accuracy of pyrometer measurements and correlate input power and susceptor temperature to sample temperature. A test plan was developed to fully characterize CFEET including pyrometer accuracy, determining do not exceed (DNE) limits. To verify accuracy of two-color pyrometers, kovar and high purity refractory metals (Zr, Hf, Nb) were melted while pyrometers measured temperature of the sample top face and susceptor operating temperature. Upon confirmation of pyrometer accuracy, the temperature difference of the susceptor and sample temperature at melt was determined to create a calibration curve of sample temperature versus input power (figure D.5).

Chemical Compatibility

Chemical compatibility of all sample holder components with the samples and each other must be demonstrated up to the highest temperatures of interest ($T > 2500\text{ }^{\circ}\text{C}$). Mass loss rate measurements are an important criterion to compare the performance and potential lifetime of candidate fuel forms. Chemical incompatibility of sample holder components and samples may result in premature sample degradation, mass gain, changes in physical properties due to chemical reaction, or contamination (figure D.6). These phenomena are undesirable as they are not representative of conditions expected within a nuclear rocket. An internal sample holder assembly, which is incompatible with the tungsten susceptor, can cause degradation of the susceptor via formation of molten compounds on the susceptor inner or outer wall during testing due to formation of low melting temperature compounds, which can lead to catastrophic failure of the assembly (figure D.7).

Conclusions

CFEET has been qualified for operation up to 2500°C for extended holds at temperatures, through the use of a W susceptor. Inert sample holder materials have been identified to enable the testing of W-matrix cermets and carbon-based ceramics at temperatures exceeding 1700°C . Future work will address readying the system for operation with radioactive materials and implementing upgraded test monitoring equipment to support testing of subscale fuels.

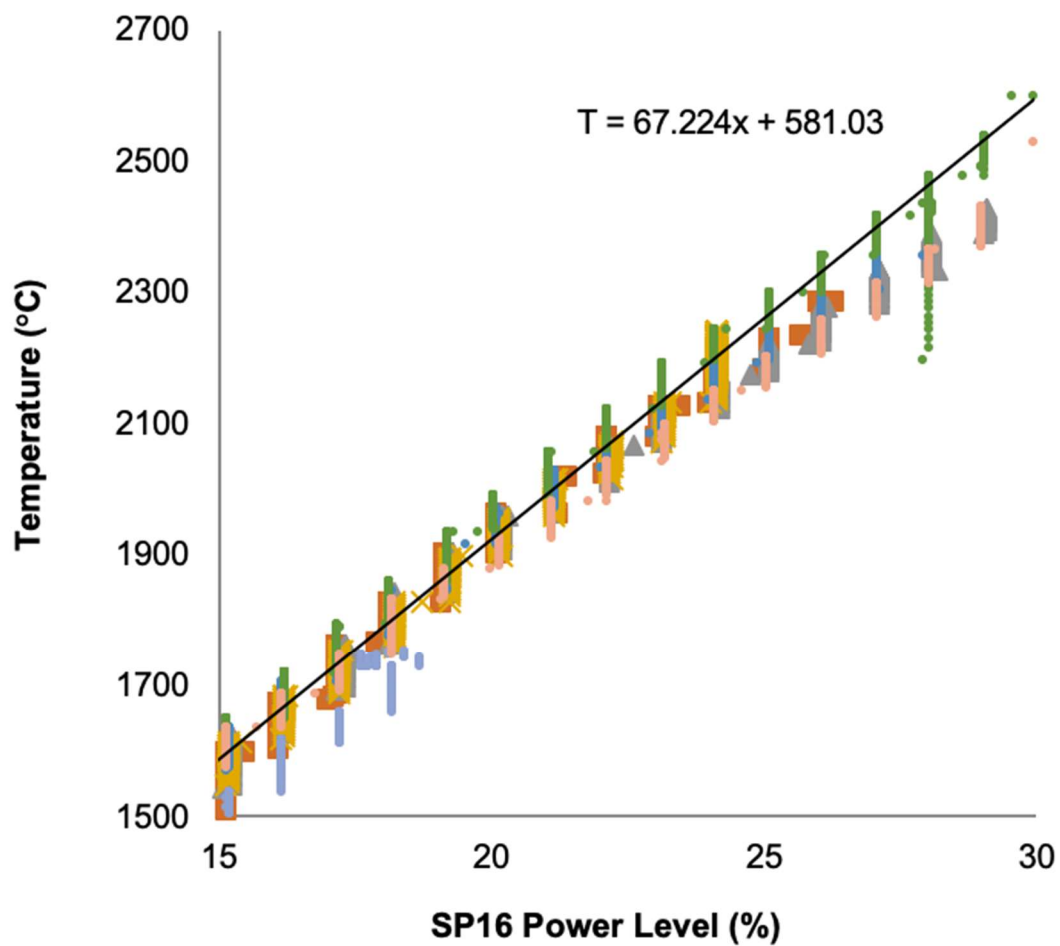


Figure D.5. Calibration curve of observed susceptor temperature dependence on SP16 input power level (%). Temperature increases with increased power input.

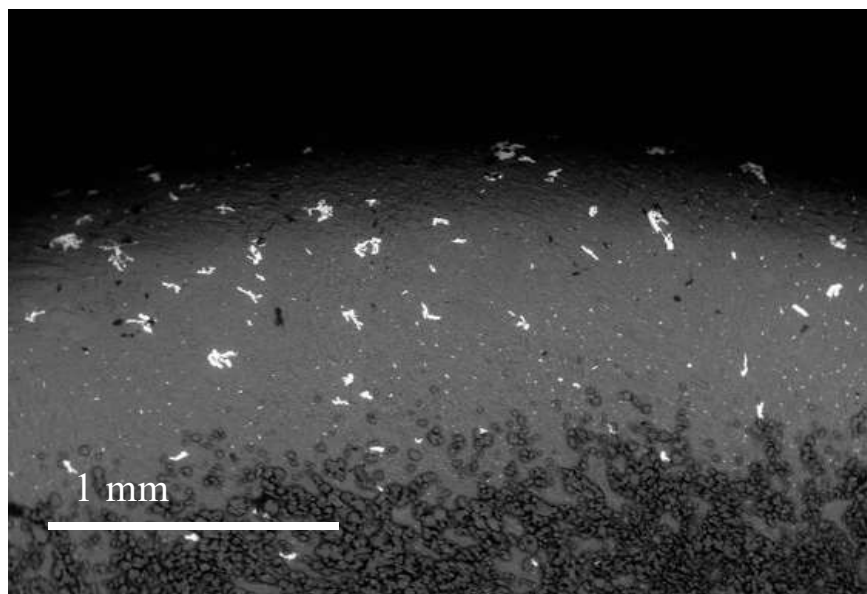


Figure D.6. Formation of molten compounds on inner wall of the susceptor may result in contamination of samples during testing(white).



Figure D.7. (Right) Example of a W susceptor operated with an incompatible SiC sample holder. Direct contact of SiC and W resulted in low melting temperature compound formation and catastrophic failure of the susceptor. (Left) Example of incompatible BN stage operated with a W susceptor which resulted in the formation of undesirable boride phases.

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VITA

Kelsa Benensky was born outside of Philadelphia, Pennsylvania on March 6, 1993. She attended the Pennsylvania State University between August 2011 – December 2014 where she graduated with bachelor of science degrees in Mechanical Engineering and Nuclear Engineering. Starting in the spring of 2015, she attended the University of Tennessee, Knoxville for graduate studies, graduating with a master of science in Material Science and Engineering in December 2016. Through undergraduate and graduate experiences at the Pennsylvania State University, NASA Marshall Space Flight Center (MSFC), and the Center for Space Nuclear Research, she was able to accumulate a diverse background in nuclear thermal propulsion including component design and development, materials processing and fabrication, test rig design and fabrication, as well as mechanical, thermal, and reactor physics analysis, which has complimented her graduate research.

Kelsa Benensky completed her Ph.D. thesis research as a NASA Space Technology Research Fellow, with primary residence at NASA MSFC. During her graduate studies, she led the re-design and qualification of the compact fuel element environmental test (CFEET) furnace which is currently utilized by NASA for verification testing of subscale fuel elements and has worked with Department of Energy staff to draft “A Preliminary Nuclear Thermal Propulsion Fuel Qualification Plan” (ORNL/LTR-2017/119). She has also participated as a research collaborator and principal investigator on several MSFC-led projects to develop and test a variety of NTP fuel forms including solid solution carbides and Mo/W cermets. The research pursued under this thesis was awarded a 2nd place award in the Advanced Fuels Category of the 2018 Innovations in Nuclear Technology R&D Awards. Kelsa Benensky is currently an aerospace engineer at NASA MSFC, where she works primarily on refractory ceramic and metals processing, testing, and characterization for the successful development of in-reactor material systems for nuclear thermal propulsion applications.