

**Corrosion and Microstructural
Characterization of Molybdenum-YSZ
Cermets Following Hydrogen
Exposure up to 2630 K**

A Dissertation Presented for the
Doctor of Philosophy
Degree

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Dedicated to my wife Lisa and children Amara and Maiben

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Abstract

Ceramic-metallic (cermet) fuels are a promising fuel type for outer space nuclear thermal propulsion (NTP). A key feasibility issue is the hydrogen chemical compatibility of candidate fuels in the proposed extreme operating temperatures for NTP systems (> 2500 K). In this study, molybdenum matrix cermets containing 40–70 vol% yttria stabilized zirconia (YSZ) particles (as a surrogate for ceramic fuel particles) were produced via spark plasma sintering (SPS) and exposed to flowing hydrogen at high temperature (2000–2630 K). Both steady state and thermally cycled (4 cycles with intermediate cooling to room temperature) conditions were examined for a constant total hot testing time of 80 min. The Mo matrix appears robust in a Mo-YSZ cermet and exhibits acceptable mass loss (< 1 wt%) with a sublinear dependence on exposure time ($\frac{1}{3}$ - $\frac{1}{2}$ power) based on hydrogen testing at 2500–2630 K with thermal cycling. Moderately higher mass losses were observed for thermally cycled (4 times) vs. isothermal specimens. The subsurface Mo-YSZ interface also remains intact despite indications of debonding at the surface. Significant hydrogen attack occurs on the YSZ grain boundaries in the interior of the samples at 2500–2630 K.

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Chapter 1

Introduction

1.1 Background

NASA’s 2018 Strategic Plan defines it’s mission to “lead an innovative and sustainable program of exploration with commercial and international partners to enable human expansion across the solar system and bring new knowledge and opportunities back to earth [1].” To achieve the broad goal of human expansion across the solar system, the NASA Technology Roadmap TA 2 (In-Space Propulsion Technologies) cites the need to develop in-space propulsion technologies that enable new missions, reduce transit time, increase payload mass and reduce cost [2]. Additionally, crewed missions beyond low earth orbit (LEO) require both high levels of thrust and high specific impulse to reduce transit time. Nuclear thermal propulsion (NTP) fulfills these requirements and is identified as one of only three technologies that will have the “broadest overall impact on enabling or enhancing missions across each class [2].” Space policy directive - 6 states that the United States will pursue goals to “Establish the technical foundations and capabilities — including through identification and resolution of the key technical challenges — that will enable options for NTP to meet future Department of Defense (DoD) and National Aeronautics and Space Administration (NASA) mission requirements [3].”

Nuclear rockets are similar to chemical engines in that they expel a hot propellant through a nozzle to produce thrust. In chemical rockets the fuel is ignited in a combustion chamber. In a nuclear rocket a low molecular weight propellant is heated by contact with a hot nuclear

reactor and is then expelled through the nozzle. A simple sketch of this process is shown in Figure 1.1. Since the 1950's there has been interest in using a nuclear powered rocket to enable a human mission to Mars. This was studied by projects Rover and the "nuclear engine for rocket vehicle application" (NERVA) program during the 1960's which included building and ground testing 20 prototype reactors [4], [5]. The primary advantage of nuclear thermal propulsion over chemical propulsion is the more efficient use of propellant. In rocketry, how efficient an engine uses propellant is defined by the specific impulse (I_{sp}) measured in seconds. High thrust primary rocket stages, like the RP-1 engines on the Saturn V, have relatively low I_{sp} (250-300s). Advanced upper stage engines like the space shuttle main engines have higher I_{sp} (450s). A nuclear rocket can achieve an I_{sp} of ~ 900 s, double that of the best chemical engines, while maintaining high thrust (10-250 klbf). This makes NTP an ideal in-space propulsion method, particularly for a mission with large mass requirements.

Historic designs from the Rover/NERVA program developed NTP systems to full scale ground tests, a technology readiness level of 6, but funding for the program was discontinued before a spaceflight test. These programs demonstrate the feasibility of NTP both as a concept and for full-scale prototype systems. A modern restart of the NTP program requires recapturing historic NTP knowledge while implementing current materials and processes to make the technology viable.

Historic NTP development was focused around minimizing reactor mass by using highly enriched uranium (HEU) in the reactor core. NASA and others have recently been investigating use of a high assay low-enriched uranium (LEU), with less than 20% ^{235}U , to achieve comparable reactor performance while reducing some of the political and regulatory requirements [6]–[12]. Using LEU as opposed to HEU may allow commercial companies to provide the fuel and more easily support the development of an NTP system as well as decrease high security costs for all handling facilities. Recently updated administrative guidelines on launch approval of nuclear systems also allow the NASA administrator to give launch approval if using low-enriched uranium fuel, as opposed to the more lengthy and cumbersome process of Presidential authorization if an HEU system is used [13]. Additionally, modern manufacturing processes such as spark plasma sintering (SPS) may be used to fabricate material systems with preferred microstructures or new types of material

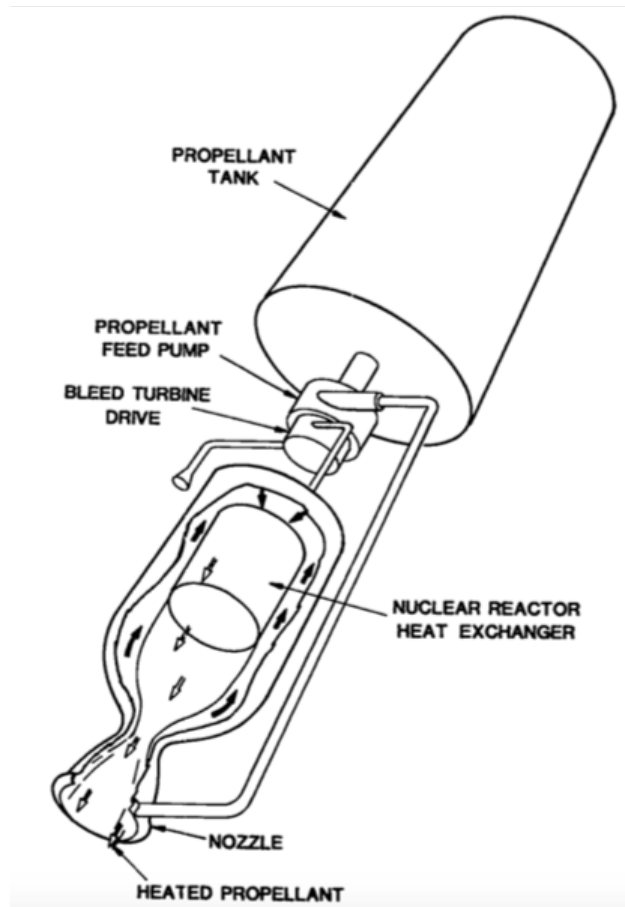


Figure 1.1: Sketch of propellant flow path for nuclear thermal propulsion [4]

systems that were unavailable in the 1960's. The purpose of this research thesis is investigate the high-temperature behavior of molybdenum ceramic-metallic fuel forms (cermets) to support the development of a LEU NTP system. This introduction covers why specific impulse matters and NTP fuel forms that have been researched in both historic and present-day programs.

1.2 Specific Impulse

Transportation in space is a balance between the thrust of the system and how efficiently it uses propellant, or specific impulse (I_{sp}). Thrust is force that can be imparted to the vehicle and determines how rapidly the spacecraft can accelerate. I_{sp} represents how efficiently the engine can use propellant and is comparable to miles per gallon of a gasoline car engine. However, unlike a car engine, rocket I_{sp} does not scale linearly and is proportional to the force of thrust over the mass flow-rate of the propellant as shown in equation 1.1.

$$I_{sp} = \frac{F_{thrust}}{\dot{m}} = \frac{v_{exhaust}}{g_0} \quad (1.1)$$

I_{sp} is derived from the exit velocity of the nozzle. Using a 1-D de Laval Nozzle to determine the exhaust velocity, equation 1.2 is produced showing that specific impulse is proportional to the square root of temperature over molecular mass. Therefore, I_{sp} is maximized when temperature is maximized and molecular weight is minimized. The highest I_{sp} chemical engines are limited by the molecular weight of the propellant (H_2O) to 450s. NTP systems can use hydrogen as their propellant and can have specific impulse from (800-1100 s) with operating temperatures above 2350 K. Figure 1.2 shows example calculations of I_{sp} for NTP systems with different propellants. Equation 1.3 defines a rocketry term called “delta V”, which is the impulse per unit of spacecraft mass that is needed to perform a rocket maneuver, such as launching from a planet.

$$I_{sp} = \frac{1}{g_0} \sqrt{\frac{TR}{M} \frac{2\gamma}{\gamma-1} \left[1 - \left(\frac{p_e}{p_c} \right)^{\frac{\gamma-1}{\gamma}} \right]} \propto \sqrt{\frac{T}{M}} \quad (1.2)$$

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

Propellant mass is the dominant mass in a rocket system. Reducing propellant mass is the best way to reduce the total mass in a given trajectory as chemical rockets may be up to 85% propellant mass with only 15% for both the payload and the structure of the rocket. High I_{sp} coupled with high thrust reduces the mass needed for propellant and thus can increase the total ΔV available, which can be used to carry more payload or to reduce time in flight from the optimal low-energy trajectory.

Reducing astronaut time in space is the major reason NTP is desired for a crewed deep space mission. Less time in space equates to reduced exposure to both cosmic and solar radiation, and reduces the adverse low gravity effects on astronauts. Chemical propulsion usually provides transit times on the order of 8-9 months for a Mars mission depending on the launch window using the low deltaV trajectory. The Curiosity rover launched in 2011 had a travel time of 253 days to Mars [15]. The added I_{sp} of NTP can reduce that time to as little as 159 days for the 2033 launch opportunity [16]. Table 1.1 shows the necessary delta V and burn time requirements for the 2033 launch opportunity [8].

High ΔV also allows for other mission trajectories; significantly it makes possible an opposition class mission as well as additional abort possibilities [17]. Typical conjunction and opposition class missions are illustrated in Figure 1.3. The current NASA architecture for a crewed Mars mission is for a conjunction class mission, i.e. the lowest energy transits between earth and Mars. This requires a long surface stay waiting for the orbital alignment for the return leg. This mission type would be valuable for a long science mission. In contrast, the opposition class mission requires significantly more *Delta V* and a Venus flyby which can add more radiation exposure but dramatically reduces the overall mission time from 3 yrs to 2 yrs. Traditional chemical propulsion can not enable a crewed opposition class mission, but with the higher I_{sp} NTP enables these missions. While an opposition class mission may not be preferred for total Mars surface time, it may be preferred to reduce total time in space and consequently reduce mission risk, limit micro gravity effects on the human

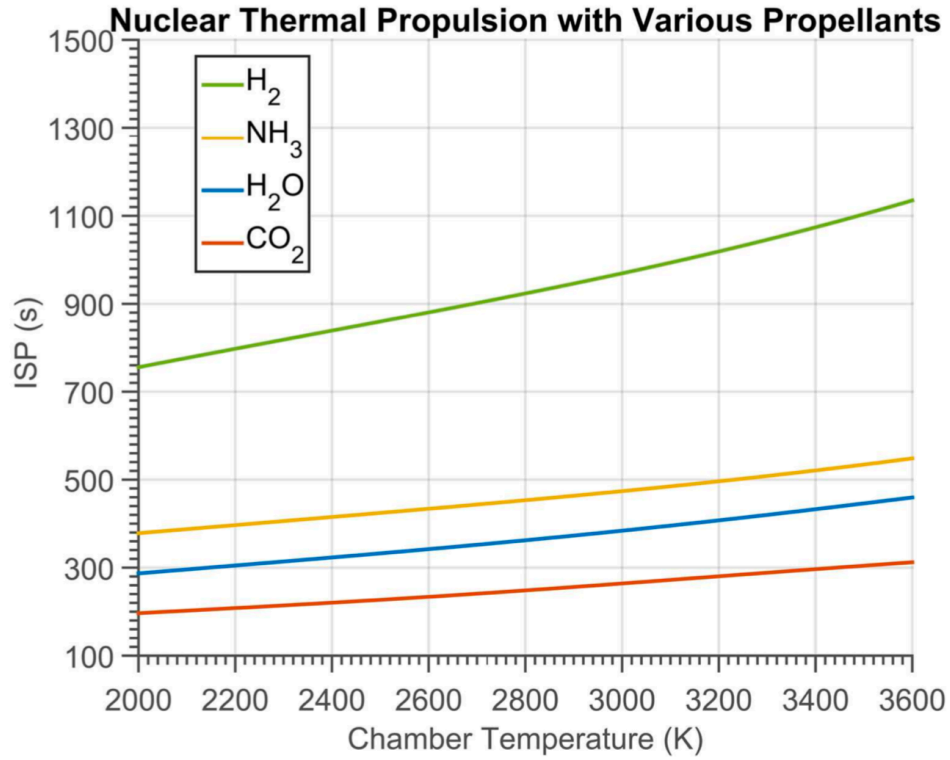


Figure 1.2: Calculated I_{sp} with various propellants. Using H₂ as the propellant specific impulse double that of chemical engines is achieved at near 2700 K. [14]

Table 1.1: NTP Primary Burns for 2033 Launch Window [8]

Burn	ΔV	Time
Trans Mars Injection	610 m/s	363 s
Mars Orbit Insertion	1648 m/s	842 s
Trans Earth Injection	1324 m/s	487 s
Earth Orbit Insertion	571 m/s	183 s

body and limit prolonged confinement of the crew. By developing an NTP system this type of mission can be considered.

While the primary driver for developing NTP is crewed deep space missions, the proposed LEU NTP system can also enable Uranus/Neptune orbiting science missions on a much shorter timeline which lowers programmatic risk [8], [18]. Additionally it can deliver over 12 metric tons of payload mass to Jupiter, 2.5 times the mass of the current Juno spacecraft, 2 years faster than that mission required without the need for gravity assists or deep space maneuvers [8], [18].

Another major option for propulsion is nuclear electric propulsion. With this technology a nuclear reactor is used to generate electricity to run an ion engine such as a Hall thruster. Ion engines can also be run using solar power. These electric propulsion methods have very high I_{sp} with significantly lower thrust. This trade is illustrated in Table 1.2. Low thrust propulsion methods are not desired for crewed missions as they do not accelerate the vehicle quickly and may require significantly longer travel times.

1.3 NTP Fuel Materials

The basic principle of a nuclear rocket is the same as a simple heat exchanger. The propellant is passed through narrow tubes in the reactor core with the goal of heating it to 2250-3000 K. Figure 1.4 shows a MCNP cross-section of a notional LEU NTP system showing hexagonal fuel elements, tie tubes containing moderator and the control drums [20]. Figure 1.5 shows both a radial and axial cross-section of notional fuel elements and tie tubes.

Similar to in-space chemical propulsion, the NTP system will need to be used for each trajectory change or burn needed for a given mission which require the reactor to be restarted. For a typical Mars mission, four burns are necessary for Trans-Mars injection, Mars orbital insertion, Trans-Earth injection and Earth orbital insertion. Reference values for single burn times for a crewed Mars mission are 5-30 minutes with total operation times between 30-100 minutes based on the mission trajectory as shown in Table 1.1 [18]. This is a short reactor operating time compared to terrestrial reactors and results in minimal burnup of the fuel. Unlike terrestrial power reactors fuel burnup is not the limiter for reactor operating time.

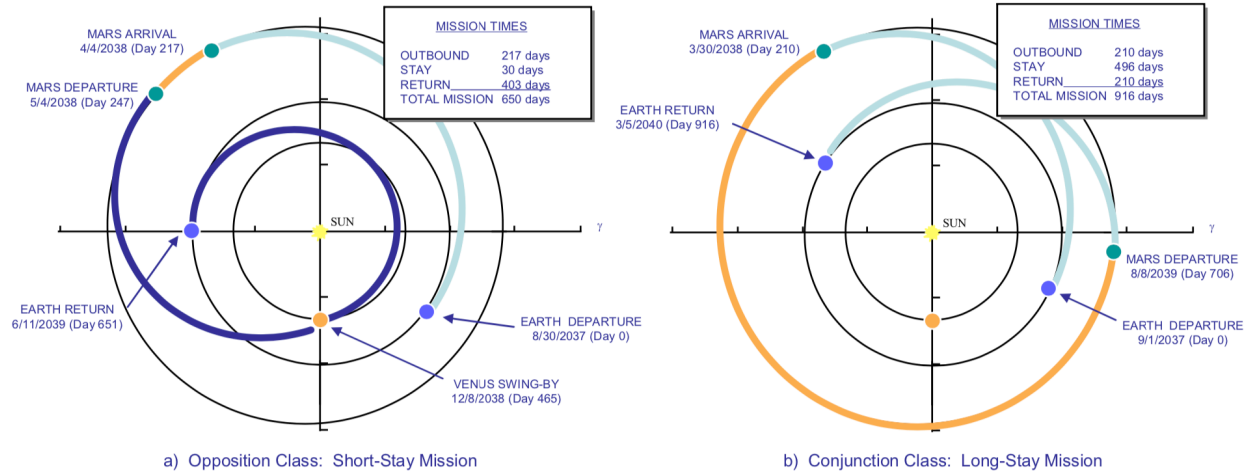


Figure 1.3: Sketch of a short-stay opposition class Mars mission and a typical conjunction class mission.[19]

Table 1.2: Propulsion Methods

Propulsion Method	Specific Impulse (s)	Thrust (klbf)	Propellant
Chemical (SSME)	452	471	LH ₂ +LO ₂
Nuclear Thermal Propulsion (solid)	800-1100	25-250	H ₂
Nuclear Electric Propulsion (Xe ion)	6000-8000	10 ⁻³ – 10 ⁻¹	Xe

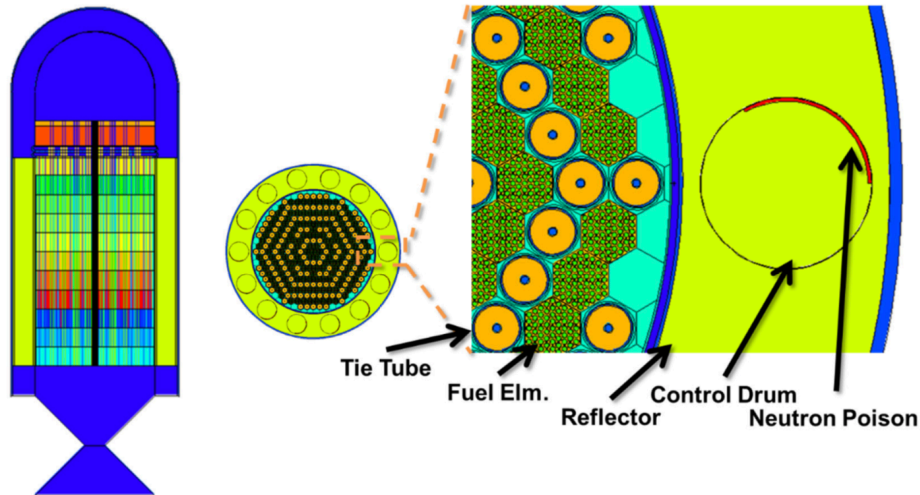


Figure 1.4: NTP geometry with a LEU design modeled in MCNP with hexagonal fuel elements and tie tubes based on the Space Capable Cryogenic Thermal Engine(SCCTE). [20], [21]

The NTP system presents a demanding environment for the fuel materials. In order to achieve the desired $900+ I_{sp}$ the nuclear reactor may have peak operating temperatures in excess of 2500 K. The material system must withstand both this high temperature as well as corrosive interactions with the hydrogen propellant. The structural integrity of the core fuel elements is also extremely important as both the mechanical loading of the system and the heat generation require maintaining a stable and durable reactor core geometry. The fuel elements thus must resist mass loss, not produce secondary phases that may compromise strength and not become unstable during the operational life of the rocket reactor. The high temperatures may produce high fuel erosion rates from surface vaporization depending on the vapor pressure of the constituent materials, or corrosive hydrogen interactions. Erosion may also be caused from thermal expansion differences between different materials within the fuel element which may include cladding, structural material, the UO_2 or UN fuel particles and any coatings. The fuel must also be able to withstand thermal shock from the rapid change in temperature when a burn initiates. Additionally, the fuel is a nuclear reactor component and so must be able to be assembled into a critical core geometry. Therefore, the amount of neutron absorption of fuel constituents is also important.

Since the first research into NTP in the 1960's several candidate fuel types have been explored including graphite based fuels, all carbide fuels and ceramic metallic fuels (cermets).

1.3.1 Graphite Based Fuels

The first materials manufactured for the NERVA and Rover programs used a graphite structural matrix. Early in the program, UC_2 or UO_2 particles were dispersed into graphite plates to form the fuel matrix. By the end of the program these had evolved to hexagonal fuel elements with a graphite matrix and a (U,Zr)C fuel web with ZrC coatings [22]. Since Rover/NERVA was the only program to build and test prototypes, graphite fuels are the only fuel type to have experienced the prototypic conditions in a full NTP reactor assembly. Graphite was selected for the NERVA/Rover programs for its high melting temperature (sublimes in a vacuum 3000 K) and these fuels are relatively easy to manufacture. Graphite also has a low neutron absorption cross-section and well understood properties and operational experience. Using graphite based fuels allows the fuel itself to moderate the

fission neutrons as opposed to exclusively relying on external moderating elements to make an epithermal or thermal neutron spectrum core which is a key advantage in designing a LEU NTP system.

The largest hurdles with graphite fuels is the inherent incompatibility with the hot flowing H_2 propellant which will rapidly form hydrocarbons such as methane at high temperature. In the NERVA/Rover programs, protective coatings such as NbC and ZrC were used to cover the graphite fuels to prevent direct exposure to the H_2 and so prevent corrosion of the graphite matrix [23]. Toward the end of the program an additional thin layer of Mo was added to enhance the effectiveness of these coatings. The major failure mechanism in these fuels occurs when there was cracking in the protective coatings allowing H_2 to penetrate and corrode the graphite matrix [4].

1.3.2 All Carbide Fuels

The transition metal carbides have very high melting points. All carbide fuels for NTP were tested at the end of the Rover/NERVA program in the nuclear furnace experiment [24]. These fuels were also investigated extensively in the soviet NTP program [25], [26]. These are in some ways an extension of the NERVA/Rover fuel types. Instead of using a graphite based matrix with a uranium carbide fuel, the matrix is also a carbide and so the entire fuel system is a solid solution of carbides. At the end of Rover/NERVA this was a (U,Zr),C solid solution. The soviet program used a variety of ternary solid solution carbides such as (U,Zr,Nb),C. Limitations of all carbide fuels include their brittleness and the low solubility of UC at high temperature which can limit high fuel loadings.

A subset of the all carbide type approach includes the coated particle type fuels developed for the Space Nuclear Thermal Propulsion Program (SNTP) in the 1980's. These fuels had a UC_2 fuel kernel, layers of graphite and a ZrC coating. The design was for spheres to be formed into a particle bed type reactor as opposed to the solid block type designs of other programs. A modern approach to all carbide fuels may be the fully ceramic microencapsulated fuels. These were originally designed as an accident tolerant fuel for terrestrial reactors and involve using TRISO type fuel encased in a solid matrix of SiC [27], [28]. One advantage of all carbide

fuels have is that the thermal expansion coefficients of the fuel materials may be more similar than for graphite or cermet fuels.

Overall the development of all carbide fuels for NTP appears promising however significantly less research has been done on these fuel forms and so they would require longer technology development. As several terrestrial advanced reactor projects and companies plan to use a HALEU in TRISO type fuels i.e.(Kairos, Oklo, USNC, X-energy), there may be programmatic overlap that could help facilitate all carbide NTP fuel development.

1.3.3 Ceramic Metallic Fuels (Cermets)

Another type of fuel considered for NTP is a ceramic-metallic composite (cermet) which has ceramic nuclear fuel, usually UO_2 or UN encased in refractory metal structural matrix, such as tungsten (W) or molybdenum (Mo). The advantage of these fuel types is that the metal matrix is inherently compatible with the hydrogen propellant in contrast to the graphite based NERVA fuels. Having a metal as the matrix material allows for better heat transfer from the fuel to the propellant compared to a fully ceramic matrix. Another key advantage with the cermet fuels is that the matrix matches the thermal expansion coefficient of the cladding, which was the major failure mechanism in the graphite based fuels. Refractory metal cermet fuel elements used for NTP do not need to maintain the reactor core in axial compression, which is a requirement of the graphite fuels; cermet fuels can instead have a single-point support at the cold-end [29].

Cermet fuel systems have been explored for a variety of nuclear space applications including both nuclear electric propulsion (NEP) and nuclear thermal propulsion (NTP) systems [29]–[31]. Through these programs, an understanding of high temperature fuel failure mechanisms and identification of optimal process parameters to extend fuel performance in a reducing H_2 environment have been determined through non-nuclear thermal cycling of candidate fuel forms and high temperature irradiation testing. Tungsten matrix, W- UO_2 , cermets have been most commonly studied through historic US NTP programs due to it's high melting point and lower vapor pressure at high temperature.[29], [30]. However limited production and test data does exist on Mo-matrix cermets originally studied for the Dumbo project headed by Los Alamos National Laboratory (LANL). NTP cermet development has

been performed at Los Alamos National Laboratory (LANL), Argonne National Laboratory (ANL), NASA Lewis Research Center, and General Electric (GE).

Limitations of W-cermets include the high neutron cross-section of natural tungsten and high ductile to brittle transition temperature (DBTT). Historic programs planned to use HEU fuel and so could overcome the high neutron absorption coefficient of natural W (18 barns for thermal neutrons). The current NASA NTP effort plans to use HALEU fuel to reduce regulatory hurdles. To create a LEU NTP system using tungsten cermets, the W would need to be enriched in ^{184}W (1.5 barns for thermal neutrons). The enrichment cost for a reactor core containing only ^{184}W would likely be quite costly. However a LEU NTP core design with W-cermet fuel has been demonstrated under the Space Capable Cryogenic Thermal Engine (SCCTE) project using an enriched ^{184}W design [21] and subsequent studies [9], [10]. These designs also use external moderating elements. An alternative is to use a Mo-based cermet. Mo has a significantly lower neutron cross-section and more easily supports a LEU core design [32]–[35]. The cross-section comparison is illustrated in Figure 1.6. Mo does have a lower melting point compared to tungsten and may limit the overall reactor temperature and thus lower the achievable I_{sp} . Mo is also less dense than W and so provides the advantage of lower mass compared to W which is highly relevant in space systems. Mo also improves ductility in the mid-band fuel regions, a relatively low temperature region of the fuel near the center of the reactor where temperature and stress gradients are highest, which have been a primary failure region in historic NTP testing [4], [36], [37].

The impetus to study cermet fuels is to have a H_2 compatible high temperature matrix containing the ceramic nuclear fuel, either UO_2 or UN. Cermets have been difficult to fabricate historically and this has limited their progression of the fuel type. No matter the fuel type chosen for NTP, modern manufacturing process will need to be employed to fabricate the fuel. Spark plasma sintering is promising as a way to fabricate cermet samples at lower temperatures than historic methods. This may result in smaller grain sizes and better mechanical properties compared to cermets developed in previous programs.

A table summarizing the key attributes and limitations of each fuel type is shown in Figure 1.7 as found in Benensky [28]. The mission requirements may dictate the fuel type chosen.

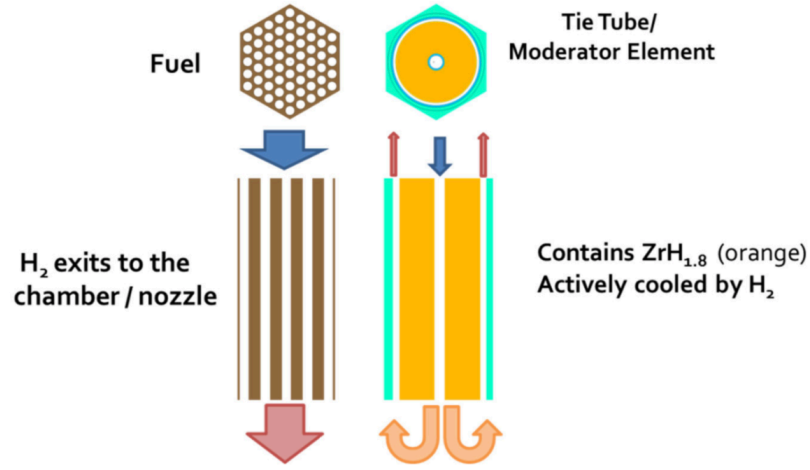


Figure 1.5: Diagram of hydrogen flow through NTP fuel elements and tie tubes. [20]

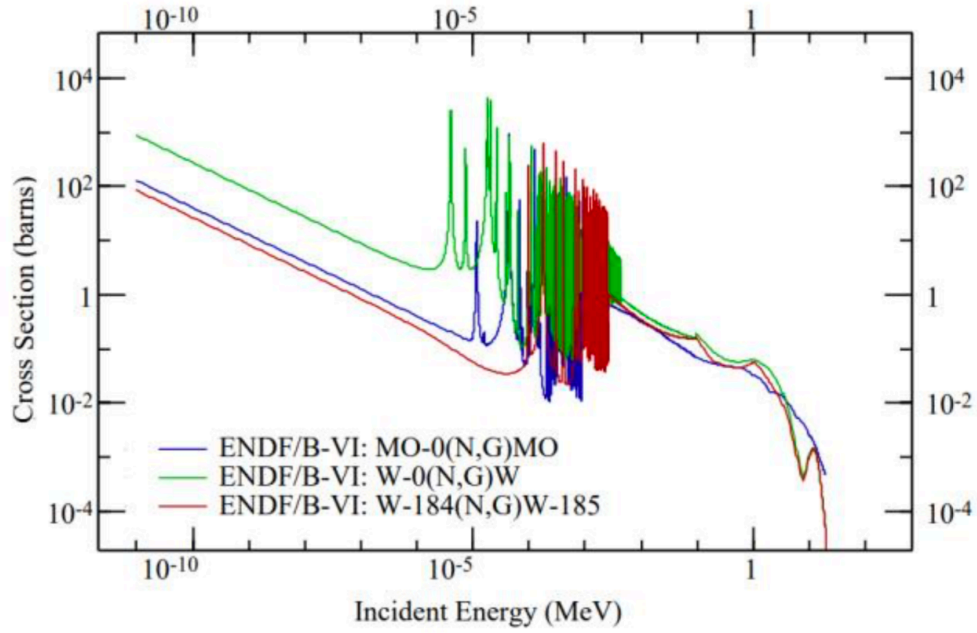


Figure 1.6: ENDF-VI radiative capture cross-sections for Mo, W and ¹⁸⁴W. [32]

1.4 Research Objectives

While all NTP fuel types have both advantages and drawbacks, cermetes are a promising candidate and a component of the current NASA NTP fuel research. The desirable qualities of Mo-cermetes include improved stability in H_2 compared to graphite, lower neutron absorption compared to W, improved ductility compared to W and lower density compared to W. These qualities make Mo matrix cermetes an attractive alternative to historic fuel systems. The relatively new spark plasma sintering (SPS) method of powder consolidation may provide improved material performance compared to limited work on Mo-cermetes in the 1960's.

The purpose of this work is to investigate the intrinsic corrosion behavior of Mo matrix cermetes at NTP relevant temperatures in a H_2 environment to inform the material selection for a future NTP fuel design. This is addressed by the major research elements described in the thesis:

- Investigate the intrinsic stability of Mo in hydrogen

Determine the intrinsic compatibility of Mo at temperatures relevant to nuclear thermal propulsion using commercially available arc-melted Mo. This will establish the base mass loss rate of the Mo in a H_2 atmosphere. This will also investigate if there is any enhanced mass loss in H_2 beyond values predicted by vapor pressure.

- Investigate the stability of a Mo matrix cermet in hydrogen

Fabricate Mo-surrogate cermetes using a powder blending method and consolidate using spark plasma sintering. Perform high temperature testing of the Mo cermetes in a H_2 atmosphere to evaluate structural stability, the importance of fuel volume loading on high temperature degradation, and whether a Mo cermet with surrogate fuel has the same degradation characteristics as those observed in W- UO_2 cermetes.

- Apply the results from surrogate material to uranium bearing systems

Evaluate lessons learned from Mo-surrogate testing to systems using Mo- UO_2 or Mo-UN

Fuel Type	σ_s (b)	σ_a (b)	Melting Temperature (K)	Key Attributes	Limiting Feasibility Issues
Cermet					
Molybdenum	5.71	2.48	2890	- 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)
Tungsten	4.60	18.3	3695		
Composite					
Graphite	5.55	0.0035	4000 ¹	- High operating temperature potential - Manufacturability - Lowest absorption cross section - Highest development status	- Chemically incompatible with hot hydrogen - Poor mechanical properties in tension
Carbide					
ZrC	12.01	0.19	3910	- 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
NbC	11.81	1.15	3770		
HfC	15.79	104.1	4250		
TaC	11.56	20.60	4250		

¹Sublimation temperature in vacuum

¹Sublimation temperature in vacuum

Figure 1.7: Comparison of historic NTP fuel types [28], [38]

Chapter 2

Literature Review

2.1 Hydrogen Corrosion in NTP

All materials experience degradation under the high temperature conditions of NTP. This can be from vaporization, corrosion, recrystallization, creep or thermal stress. Fuel material candidates must mitigate these degradation mechanisms to have acceptable performance.

A significant technical challenge under the NERVA/Rover program was fuel degradation. The graphite matrix was selected due to its high temperature properties and ease of manufacturing. However mitigating the fuel loss from the graphite with the highly reactive H_2 propellant was a major hurdle. The NERVA/Rover program used various protective coatings to mitigate the H_2 /graphite interactions and subsequent fuel loss by impeding direct contact between the fuel and the propellant. The structural matrix was protected by these coatings including NbC and ZrC, with the high temperature regions having reduced corrosion rates [23]. Near the end of the program a thin layer of Mo was added on top of the ceramic coating for additional protection. The maximum corrosion rates occurred in a moderate temperature zone (~ 1500 K) dubbed the ‘mid-band’ region as shown in Figure 2.1. The cited reason for increased corrosion in the mid-band region is increased cracks in the coatings due to the mismatch in the thermal expansion coefficients between the matrix and the coatings [23]. However this was also a region of high power and the region that may have experienced the most irradiation hardening both of which may have contributed to greater fuel loss. The authors also noted that fission fragment damage accelerated the

degradation of the carbon matrix [24]. The final fuel designs at the end of the NERVA/Rover program consisted of a graphite matrix with a dispersed (U,Zr)C fuel web and a ZrC coating, and an alternate all carbide design using solid solution (U,Zr)C for the full fuel element also with ZrC coatings. This limited mid-band corrosion to $45 \frac{mg}{m^2s} \approx 16.2 \frac{mg}{cm^2hr}$ [4]. Modern fuel development for NTP must have lower mass loss than this peak rate.

2.2 Cermet Corrosion for NTP

Haertling summarizes much of the literature on cermets fuels for NTP including their relevant failure mechanisms: fissile fuel loss and loss of mechanical integrity [40]. Most degradation information for cermets from past testing has been learned from W-UO₂, however similar degradation mechanisms have been observed for Mo-UO₂ cermets as well. Fuel on the surface is preferentially lost by high temperature vaporization of UO₂. Interior (bulk) UO₂ fuel is lost due to reduction of UO₂ to sub-stoichiometric UO_{2-x} at temperatures exceeding 1400 °C, see the phase diagram in Figures 2.2, 2.3 and the micrograph in Figure 2.4. The free uranium (U) and oxygen (O) products subsequently migrate by grain boundary diffusion. During cooling, free U can then react with O in grain boundaries to reform UO₂ or react with hydrogen to form UH₃. Volume changes associated with this process weaken matrix mechanical integrity. Thus, thermal cycling produces significantly more fuel mass loss than a single run at high temperature for the same total duration. This proposed mass loss mechanism is shown in Figure 2.5. If the UO₂ is exposed at the surface it has high surface vaporization in addition to the described bulk loss mechanism.

Fuel mass loss is exacerbated by cracks, impurities, and interconnected fuel particles. Fuel properties such as higher ductility (due to reduced grain size or Re additives), high theoretical density, particle coatings, and UO₂ additives (Y₂O₃), as well as protective cladding have been shown to increase fuel performance and prevent loss of mechanical integrity during hot hydrogen testing. Test conditions such as a hydrogen environment (compared to inert atmospheres or vacuum) and increasing test temperature, gas flow rate, and pressure have been shown to greatly increase UO₂ mass loss. To reduce mass loss, stabilizers were also included in the UO₂ such as ThO₂, Gd₂O₃, and Y₂O₃. These helped mitigate the oxygen

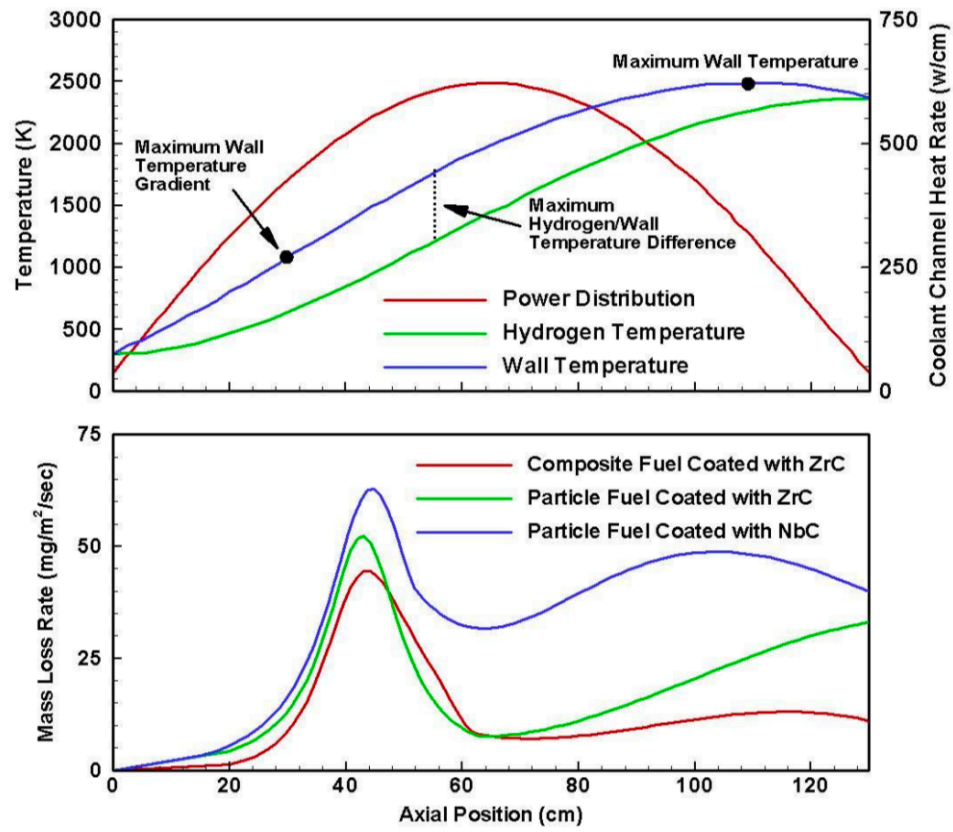


Figure 2.1: Mass loss behavior in graphite based fuel elements from the NERVA/Rover programs. [4], [39]

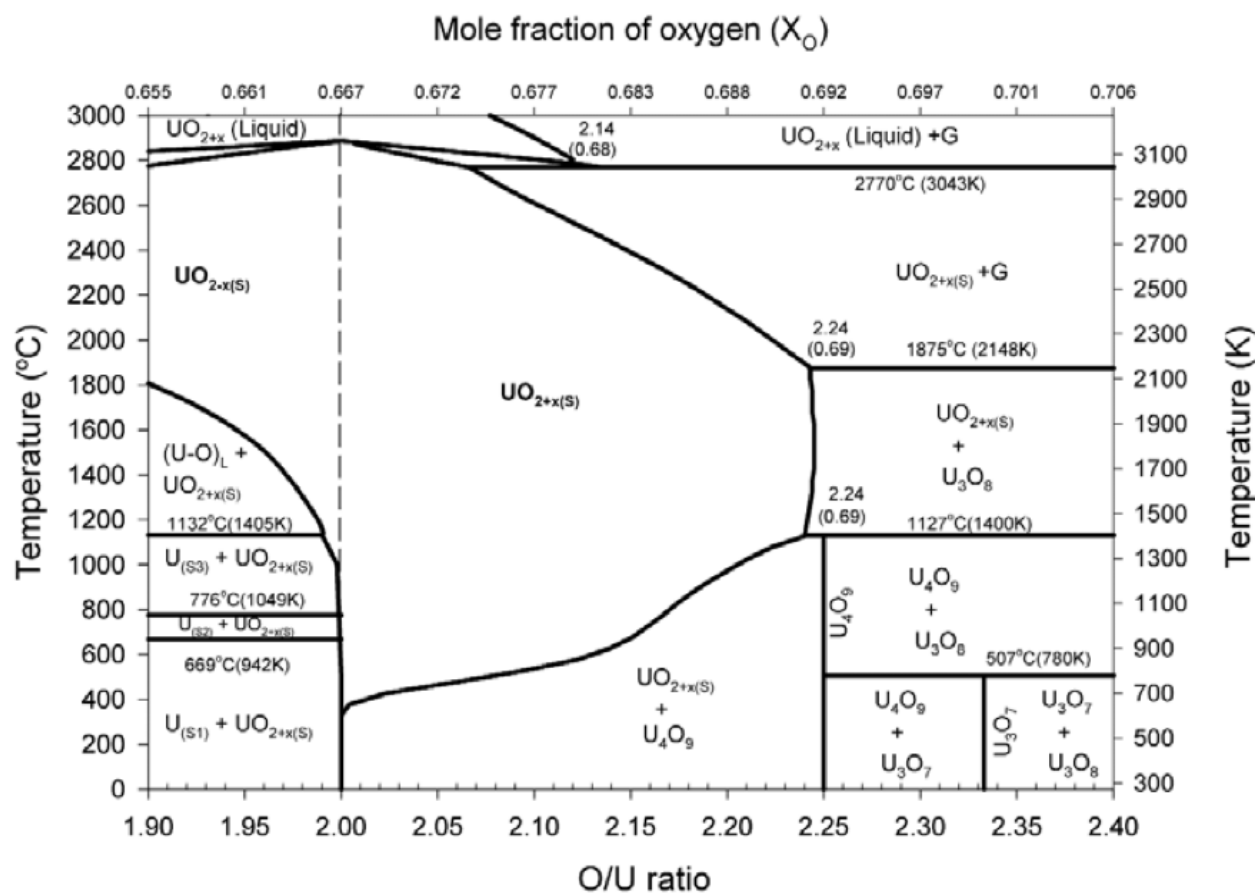


Figure 2.2: UO_2 phase diagram as a function of the U/O ratio [41]

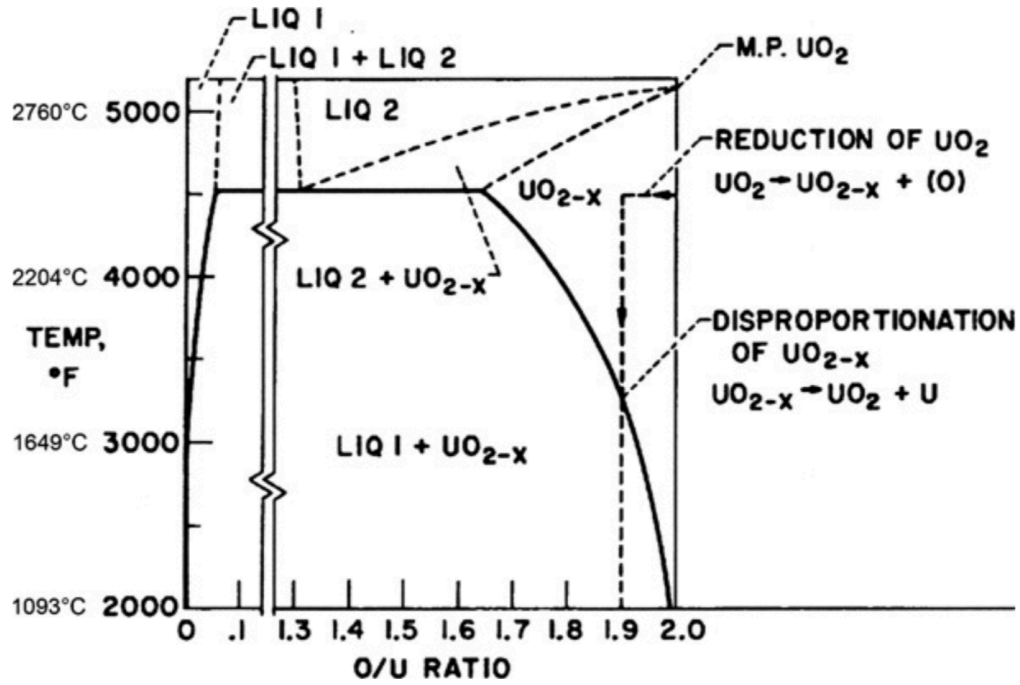


Figure 2.3: Portion of the UO₂ phase diagram that is relevant for cermet fuels showing the UO₂ reduction with temperature.[40], [42]

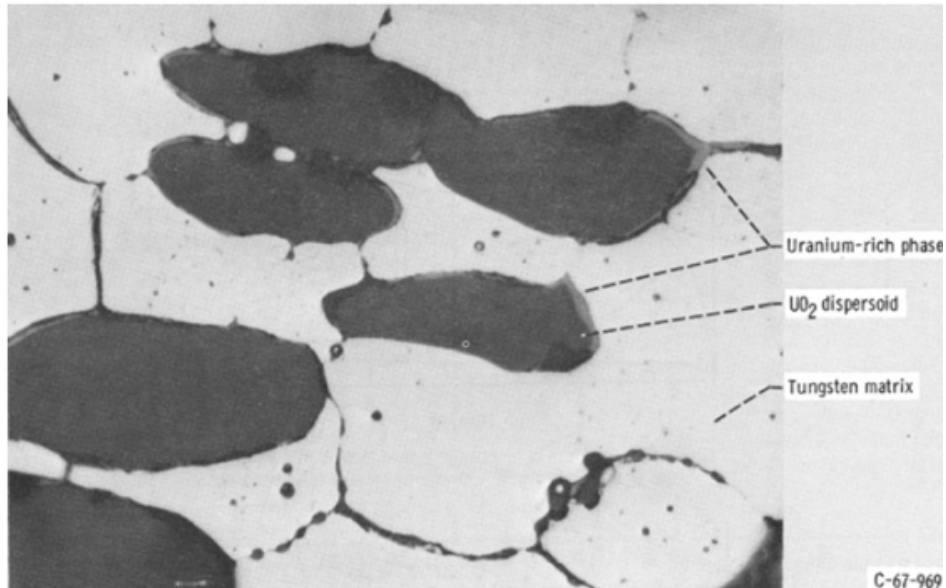


Figure 2.4: Micrograph of thermally cycled W-20 vol.% UO₂ cermet showing free U at grain boundaries. The specimen was heat treated for five 1-h intervals at 2500 °C in H₂ with cooling to room temperatures between cycles[40], [42]

depletion of the UO_2 . The mismatch of the thermal expansion coefficients between the ceramic fuel and the metal matrix can cause significant stress during thermal cycling and may produce cracking. Highly mismatched grain boundaries ($> 45^\circ$) have been a concern in previous W- UO_2 development [43].

2.3 Mo Cermet Studies for NTP

Initial development of Mo-matrix cermets for very high temperature propulsion applications took place at LANL to support the NERVA/Rover project in the Dumbo program. Lenz and Peterson thermal cycled (10 minute typical dwell time) Mo-20-25 vol% UO_2 hot rolled and sintered cermet foils both in vacuum and unpressurized H_2 environments at maximum test temperatures of 2100 and 2280 °C respectively (2373, 2553 K) [31]. Theoretical densities of 98-99% could be achieved for sintering dwell temperatures of 1700 °C using TiO_2 additives to form a liquid oxide phase. Preliminary testing results showed that higher %TD specimens exhibited reduced mass losses in high temperature hydrogen (2553 K) and vacuum (2373 K). Mo cermets with ThO_2 additives were also observed to correspond to the reduced mass loss. ThO_2 was thought to reduce grain growth during sintering and help retain ductility of the cermet matrix. Temperature and hydrogen played a greater role in influencing mass loss than low vapor pressure in low temperature vacuum testing. Mo-cermets lost 5-10 wt% mass in a single hot hydrogen test at 2300 °C for 10 minutes and 1-6 wt% in vacuum in 10 minute tests at 2100 °C. Samples with higher area to volume ratios lost more mass. Mass losses of standardized Mo-cermet specimens tested for 10 min in hot flowing hydrogen up to the melting temperature of Mo were also reported. Mass loss was limited to less than 10 wt% for test temperatures less than 2600 K. Mo vaporization was determined to be lower than UO_2 losses at test temperatures of 2280 °C (2553 K) and lower. High temperature, uncoated UO_2 loss rate is the highest in the first 0.5-2 min of testing due to preferential vaporization at the surface of sample coupons.

Ranken summarized completed irradiation testing on Mo-40 vol% UO_2 cermets with a W clad [44], [45]. 39-88 temperature cycles were performed with average pin maximum irradiation temperatures of 1900-2100 K. These samples were tested to a maximum ^{235}U

burnup of 36.8%. They created a microstructure model based on micrographs and porosity measurements. Their mass loss model as a function of time is derived from samples at 1900 °C (2170 K) in vacuum. Small changes in porosity were observed to have a large effect on fission gas escape rate and diametric sample growth due to solid and gaseous fission product formation. Minimal fission product damage was observed after 3000 hr neutron irradiation at 240 W/cm³.

Later in the development of cermet for nuclear space applications, Lenz and Munding tested several W-Mo-Re alloy cermet at temperatures of 2100-2600 °C in an H₂ environment [46]. Thermal cycling allowed U₂ dissociation at high temperatures with U precipitating along particle interfaces and grain boundaries after cooling, which was confirmed by later studies. Cracking was observed to increase with increasing UO₂ loss. However, even a loose W foil clad greatly reduced mass loss, as the surface then has much less contact with H₂. This testing also observed increased mass loss trends with increasing temperature and hydrogen thermal cycling. Evidence shows that the hydriding reaction is accelerated at high temperature leading to mass loss for samples in flowing H₂ when compared to using He gas at high temperature and only H₂ during cooling.

Other NTP cermet fuel programs that are included in the summary by Haertling include the Argonne National Lab Program [30], the GE 710 program, which includes some limited testing of a Mo-60UO₂ cermet with Mo-50Re cladding [29], the NASA Lewis Research Center Program [47], [48] and development during the Space Exploration Initiative (SEI) program [49].

While Mo-cermet have been observed to exhibit similar failure mechanisms as W at moderate temperatures ($T < 2200$ °C), Mo vaporization has been shown to enhance fuel mass loss and loss of cermet mechanical integrity at very high temperatures [31], [50]. Thermodynamic data for Mo shows its vapor pressure at 2500 K is 6.61×10^{-7} atm and at 2745 K is 10^{-5} atm [51]. The significant change in vapor pressure leads to increased vaporization at higher temperatures. This vaporization has the potential to lead to enhanced mass loss and a recession of the Mo matrix at the fuel-coolant interface, thereby exposing interior fuel particles or leading to changes in thermal-mechanical loadings of the fuel which

can result in matrix cracking to further enhance mass loss. This effect has been observed to be more important for Mo than W.

Modern production methods including using spark plasma sintering (SPS) to consolidate the cermets as opposed to hot isostatic press (HIP) methods may increase the performance properties of both W and Mo cermets. The SPS process passes a DC current through a powder mixture while applying uniaxial pressure resulting in Joule heating. The heating is controlled through current pulse modulation which is used to raise the powder mixture from set operating temperature to a much higher localized temperature in each current pulse [52]. During a current pulse, material is transported by a plasma across pores of the matrix. While the pulse is off, the matrix cools rapidly, and this lead to condensation of the material vapor within regions where there is mechanical contact between grains. This mechanism leads to necking between grains [53]. SPS allows for consolidation at a lower average temperature than is needed for HIP which helps give a product with a smaller grain size and limit reduction of UO_2 . In historic programs, cermet fuels needed to be sintered at 2200 °C [47], while SPS methods may bring down the temperature to 1400-1700 °C.

Work by Tucker on uranium migration in W- UO_2 cermets [53], [54] found that the UO_2 was substoichiometric following sintering at 1600-1700 °C. Their conclusion was that the uranium had migrated into the W. The W- UO_2 boundaries look clean in most samples, but they did find an anomalous phase with $\text{U}_{0.1}\text{WO}_3$ which may just be WO_3 with some uranium contamination.

2.4 Molybdenum Metal Properties

Most of the published literature for Mo use in H_2 is limited to 1300°C [55]. Mo does not have strong chemical interactions with hydrogen at high temperature. Hydrogen can even be used similar to an inert gas for Mo heat treating [56]. Mo powders are usually heat treated in hydrogen to remove oxides prior to sintering including for the Mo-ceremts developed by Lenz et. al. [31]. Birnbaum claims that Mo and W alloys are generally considered to be unaffected by hydrogen as they do not have stable hydrides, and have low hydrogen solubility [57]. Their study showed no embrittlement with tension tests by room temperature exposure

to a H₂ atmosphere at 5 psi. They showed some embrittlement at room temperature when using cathodic charging of the Mo with a H₂SO₄ electrolyte. Because the terminal solubility of H in Mo and W is “extremely low” it is often not included in comparison plots even when the solubility of other refractory metals are discussed [58].

Caskey studied the reversible trapping of hydrogen in internal material defects. They define an equation for permeability of hydrogen in Mo in the temperature range of 523-730 K. $\phi = 3.22 * 10^{-4} \exp\left(\frac{-19828 \text{ cal/mol}}{RT}\right)$. They studied hydrogen trapping by saturating the Mo with tritium and then producing a radiograph. The trapping of hydrogen by dislocations is concluded to be significant [59]. Many other authors have discussed the diffusivity and permeability of H in Mo including Katsuda and Oates. [60], [61] Oates states that at 1521 °C the H/Mo atom ration is $12.63 * 10^5$, and at 905 °C atom ratio is $2.136 * 10^5$ [61].

An equation for H₂ diffusivity is given by Tanabe as [62]

$$D = 4.0 * 10^{-8} * \exp\left(\frac{(-22.8 \text{ kJ/mol})}{RT}\right) \left(\frac{\text{m}^2}{\text{s}^{-1}}\right)$$

Using the data from several authors [63], [64] Abramov constructed a phase diagram of Mo-H formation as shown in Figure 2.6 [65]. The α -phase is the diluted hydrogen solution in the bcc metal, the ϵ -phase is the Mo-hydride high-pressure low-temperature hcp phase, and the γ -phase is the high temperature Mo-hydride with fcc structure. This diagram does not quite extend to the region of interest for NTP i.e. high temperature and relatively low pressure. This work does not show any type of Mo-hydride phase at lower than 2.2 GPa. The notional NTP system will likely run at 6 MPa of hydrogen pressure. Belash produced a Mo-hydride at 6 GPa and 350°C but noted that after quenching it is unstable at room temperature and pressure [66]. Kuzovnikov created a nonstoichiometric molybdenum hydride at a pressure of 4 GPa. When the phase transformation was observed from the bcc metal to a hydride with a hcp metal lattice the H/Mo ratio was 1.1. [67]

Another concern for both W and Mo cermets is their ductile to brittle transition temperature (DBTT) because of the body centered cubic (BCC) crystal structure of both Mo and W. Due to the BCC crystal structure, there is a higher activation energy for dislocation motion. At high temperature, stress in BCC materials can be relieved by dislocation motion. At low temperature, the dislocations cannot move due to the high activation energy and so the stress results in brittle fracture. This is an important quality when considering BCC

materials such as Mo and W, particularly in the context of harsh thermal cycles where the temperature will likely go below the DBTT between burns. Depending on the fabrication process and the testing direction the unirradiated DBTT of Mo ranges between -150 and 200°C [68]. The DBTT will also elevate under neutron irradiation in the portions of the fuel below 600-800°C [69] and can elevate as high as 400°C over the unirradiated values. However other candidate NTP materials, like all carbide fuels, are also very brittle despite not having a DBTT. Additionally, Mo is more ductile than W and so may have advantage over traditional W-cermets.

Some reviews of Mo cermets for NTP have dismissed Mo as a candidate refractory metal for NTP cermet fuels because it has a higher vapor pressure than W [50]. Comparing the thermodynamic data of Mo and W pure metals, it is expected that Mo cermets may have more matrix volatilization than W cermets [56], [70]. Thermodynamic data for Mo shows its vapor pressure at 2500 K is 6.61×10^{-7} atm and at 2745 K is 10^{-5} atm [51]. One of the goals of this study aims to test this extrapolation to cermet materials and whether enhanced matrix vaporization leads to decreased fuel performance. Hubble gives a good standard reference for the x-ray diffraction pattern of Mo [71] which is compared to the XRD patterns collected in this study.

2.5 Yttria-Stabilized Zirconia Properties

Yttria-stabilized Zirconia is high-temperature compatible material with diverse applications including as a structural ceramic [72], an electrolyte for high-temperature solid-oxide fuel cell (SOFC) applications [73], thermal barrier coatings in gas turbines [74], as a support structure for various catalysts [75]–[77] and as a surrogate for uranium fuels (UO_2 and UN) [78], [79].

While the primary goal was to use the YSZ behavior to better understand potential changes that might occur in a uranium bearing system, the results of high temperature hydrogen compatibility with YSZ may also be useful for other applications that would involve compatibility with hot hydrogen. ZrO_2 is considered to be a 'nonreducible oxide' in H_2 with little evidence of Zr metal formation even at high H_2 pressures and at 2500 °C [80], [81], more similar to MgO and SiO_2 than to TiO_2 or CeO_2 [82]. Instead the substoichiometric

oxide, ZrO_{2-x} , is formed. According to computer simulations, $\text{ZrO}_2 + \text{H}_2 \rightarrow \text{ZrO}_{2-x} + \text{H}_2$ is endothermic with a reaction energy of 3 eV [11]. Previous work with YSZ reactions in H_2 are less common than for ZrO_2 [75], [83] and have focused on lower temperatures (1000°C).

In this study, yttria-stabilized zirconia (YSZ) is used as a surrogate material for UO_2 . In contrast to UO_2 , YSZ has fewer phase boundaries at high temperature. This is illustrated by the phase diagram in Figure 2.7.

The reason that zirconia has the addition of the yttria is to maintain the tetragonal phase and prevent a room temperature transition to the monoclinic phase [84]. The transformability of the YSZ crystal decreases with increasing yttria concentration [84] as it increases the t to m phase transition temperature. In addition to the nonreducible nature of ZrO_2 it also contains a stabilizer (yttria). Consequently the zirconia may be less likely to reduce in a hydrogen environment than pure UO_2 and may not follow the classic degradation behavior in a NTP cermet; such as free metal formation in the grain boundaries and subsequent hydride formation. However, most NTP cermet fuel research agrees that the addition of a stabilizer to the UO_2 in a NTP cermet fuel is necessary to reduce these effects. YSZ used in this study is 5.1wt% yttria and in the tetragonal phase at room temperature. Based on the phase diagram, some amount of cubic phase may be present following high temperature testing.

Cubic phase evolution of a 7-8% yttria YSZ annealed at 1300 °C did not occur until 100 hr of annealing as shown by the emergence of the XRD peak at 73.5 °as seen by Witz [74]. Their XRD step size was 0.01°. The system starts in t' phase and at 10 hrs has very slight indication of both t and c phase. After 1000 hrs the t' phase disappears completely. Prepared with atmospheric plasma spray and then annealed at temp. Only when the yttria depleted regions reach a critical size do they undergo the martensitic transformation to the monoclinic phase There are different tetragonal phases based on the amount of Y content, i.e. the lattice parameter changes slightly. Their bounds are t (4-5%), t' (7-8%). But the decomposition rate of the t' phase scales by an order of magnitude with every 100 K change in temp. They note that Y diffusion is fast and that it can be hard to resolve the different peaks in the 72-76 °region.

Tetragonal to monoclinic volume change is about 5% this transformation may be stress induced as seen by Gupta[85]. Butz et al saw tetragonal precipitates in the cubic matrix under TEM [86]. Their 8% YSZ was not fully cubic, it had t'' phase on the order of 1 nm. At 1000°C for 5000 hr these coarsened to 5-10 nm. After 2500 hr at 950°C had alternating depleted and enriched phases 4% and 10% Y.

Data on the thermal and mechanical properties of zirconia varies based on the amount of yttria used as a stabilizer. Publications such as Nielsen [87] give thermal expansion data over a broad range of temperatures, from 200-2200°C with values ranging from $9 - 13 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$, however this data is for 15% yttria. These values may be overestimating the thermal expansion based on other sources for the 6% yttria. Others such as Tsukuma show that a 6% yttria zirconia will not increase its thermal expansion coefficient above 10×10^{-6} up to 1600 °C [88]. Other work by Hayashi cites the Tsukuma values as 10% too small [89]. Terblanche states that the thermal expansion coefficient should be independent of the yttria content if the YSZ is in the cubic phase [90]. YSZ with lower amounts of yttria to only stabilize the tetragonal phase (2-9 %) as opposed to cubic YSZ has higher fracture toughness [91], [92].

Kim gives a good reference for the 6% YSZ x-ray diffraction pattern [84]. Witz also gives good examples of phase evolution in the YSZ from tetragonal to include some cubic phase as shown by XRD [74]. Both of these are compared to the XRD patterns collected in this study.

Lughi and Clarke test the low temperature transformation to monoclinic phase[93]. At high temperatures, the meta-stable tetragonal prime phase slowly transforms to a mixture of three phases: A cubic phase, a yttria-rich tetragonal phase (t') and a yttria-poor tetragonal phase. The rate of these transformations is determined by the rate of yttrium-ion diffusion [93].

The shift from tetragonal to monoclinic phase in YSZ is common under low temperature and some water vapor, it has even been noted in come cubic YSZ [94]

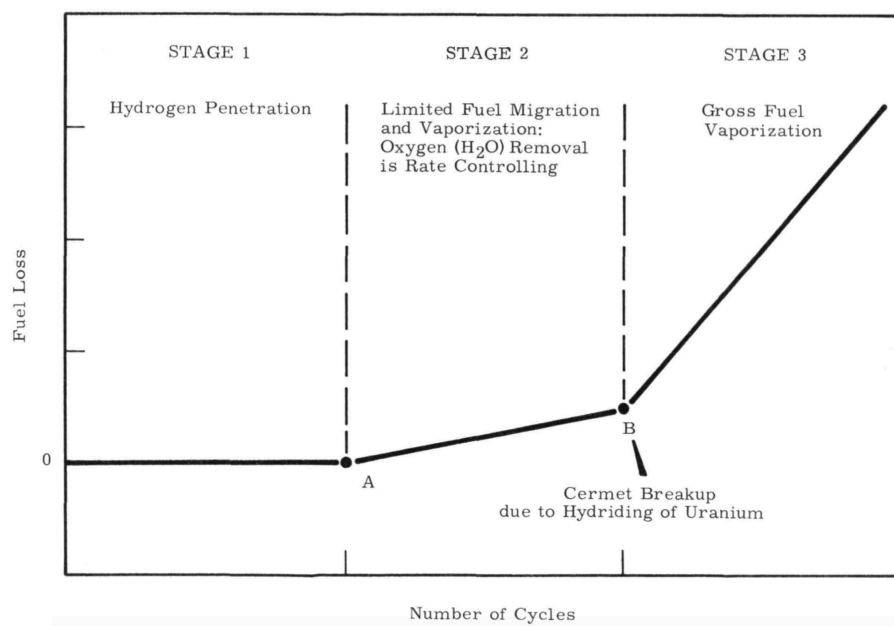


Figure 2.5: Proposed mechanism of thermal cycling behavior of W-UO₂ cermets [43]

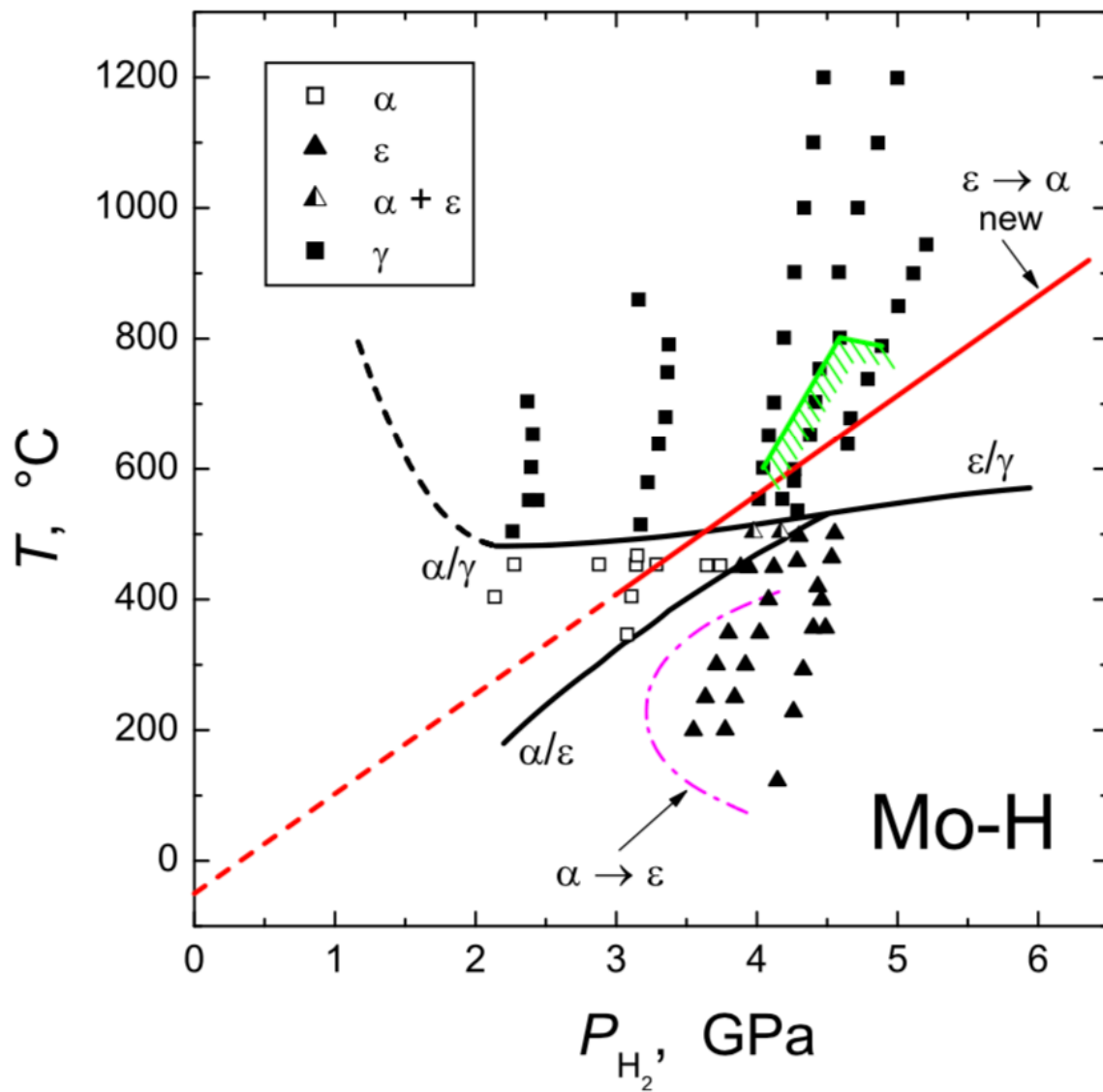


Figure 2.6: Phase diagram of the Mo-H interaction showing the conditions for the α phase (H soluble in bcc Mo), the ϵ phase (Mo-hydride high-pressure low-temperature hcp) and the γ phase (high temperature Mo-hydride with fcc structure) [64], [65].

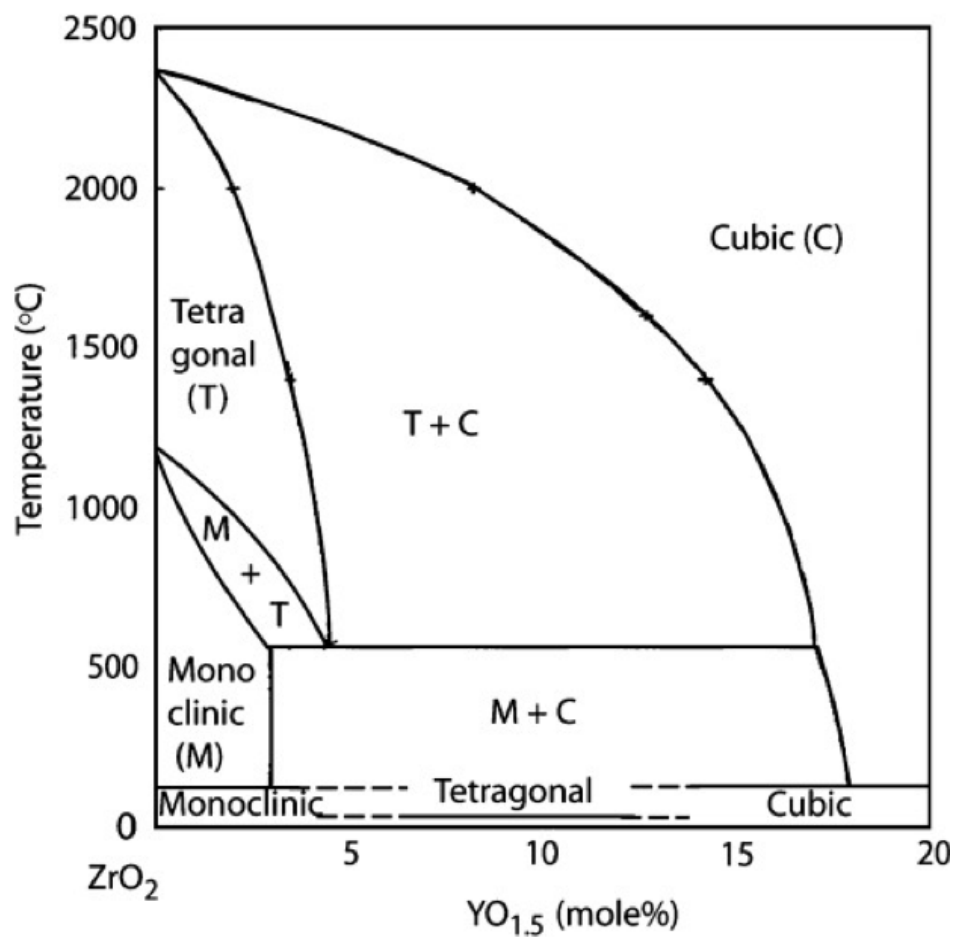


Figure 2.7: YSZ phase diagram as a function yttria fraction [74]

Chapter 3

Thermodynamics Calculations

Gibb's free energy calculations were performed to predict corrosion products for the Mo-YSZ system in hydrogen. These calculations were performed using the Equilib-Web thermodynamic software which uses the FactSage database for pure substances[95]. This database only considers pure solids, liquids and ideal gas phases and does not consider charged species or non-ideal solutions. A series of calculations was performed on four systems considered in this work Mo+YSZ+H₂, YSZ+Al₂O₃+H₂, Mo+UN+H₂, and Mo+UO₂+H₂. Al₂O₃ was evaluated since it was used as a minor sintering aid in the YSZ particles, and UN and UO₂ were included due to their importance as prospective particle fuels in the cermet. The basis of the calculation was reacting 10 moles of the solid reactants (Mo+Fuel) with 1 mole of H₂ over a temperature range of 1750-2750 K. For calculations with YSZ the 10 moles was split into the relative mole fraction of each constituent (e.g., 9.68 mol ZrO₂, 0.285 mol Y₂O₃ and 0.031 mol Al₂O₃).

Figure 3.1 shows the plot for the Mo-YSZ system without including the alumina while figure 3.2 shows the YSZ system with alumina but without the molybdenum and is most extensible to other high temperature YSZ applications in H₂. Comparing these two figures it is important to note that even the small quantity of alumina increases the equilibrium concentration of water vapor by 2 orders of magnitude and introduces many other Al-products in higher concentrations than the Mo-YSZ system alone. Additionally, while not shown in these plots, if Al₂O₃ is added with the Mo, the various Mo-oxide concentrations can reach the 10⁻⁵-10⁻⁶ range at 2750 K.

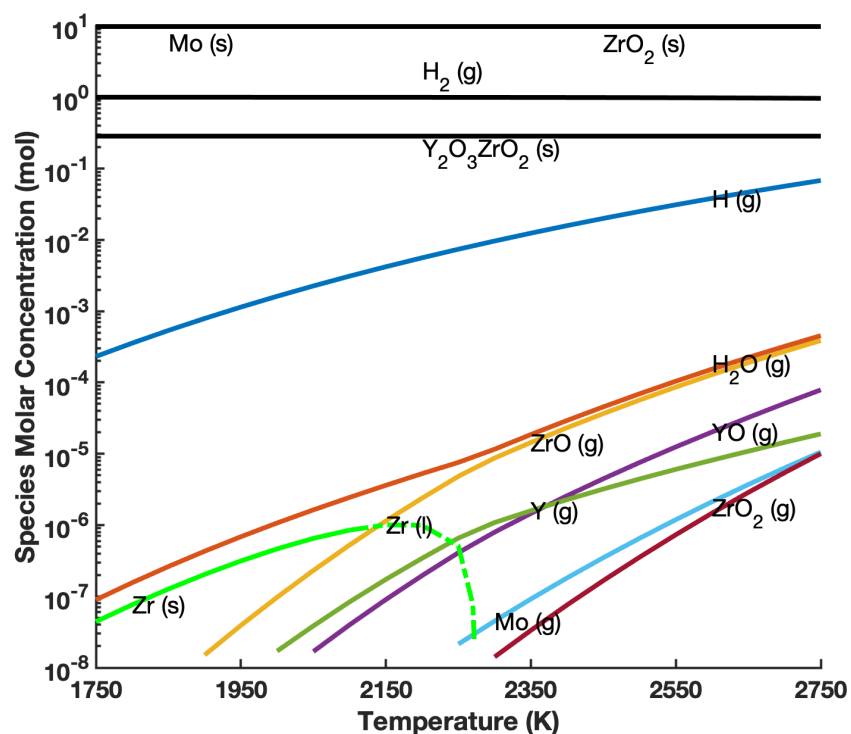


Figure 3.1: Predicted thermodynamic stability of Mo-YSZ in hydrogen with primary corrosion product species. Gibbs free energy minimization calculations were performed using 10 mole Mo, 9.68 mole ZrO_2 , 0.285 mole Y_2O_3 and 1 mole H_2 reactants at a pressure of 1 atm for temperatures of 1750- 2750 K

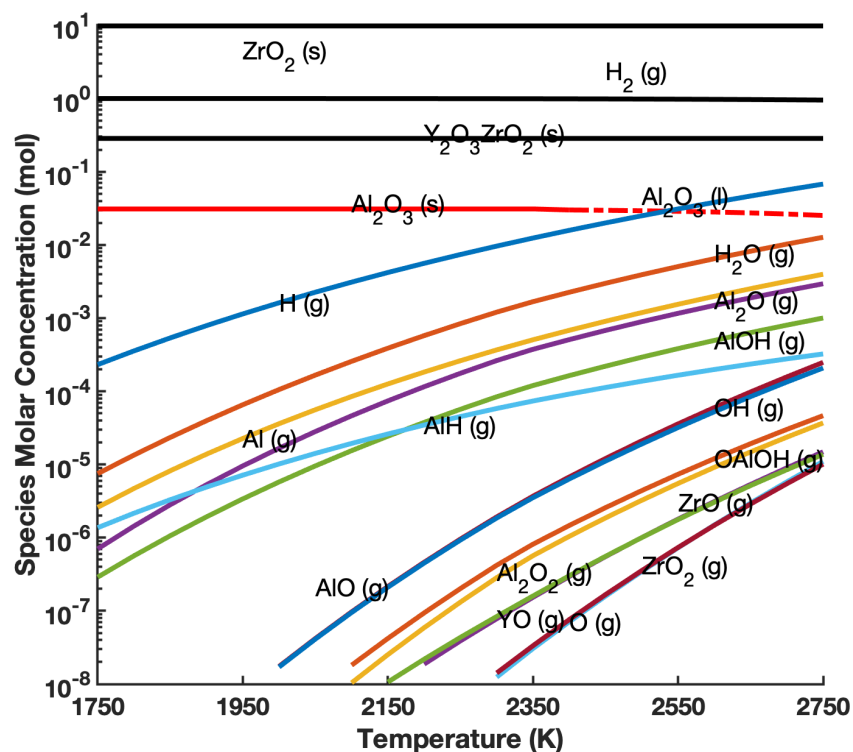


Figure 3.2: Predicted thermodynamic stability of Mo-YSZ in hydrogen with primary corrosion product species. Gibbs free energy minimization calculations were performed using, 9.68 mole ZrO_2 , 0.285 mole Y_2O_3 , 0.031 mole Al_2O_3 and 1 mole H_2 reactants at a pressure of 1 atm for temperatures of 1750- 2750 K

Figure 3.3 and 3.4 show similar systems of Mo and H_2 with UN or UO_2 . For UN there are high U (liquid) and N_2 concentrations are several orders of magnitude higher than any YSZ metal or oxide component. The UO_2 results are much more similar to the YSZ system as long as Al_2O_3 is excluded. Gibb's free energy calculations do not provide information about kinetics of reactions or about transport of species through the sample to the surface, however they are useful to see what species may evolve in the system.

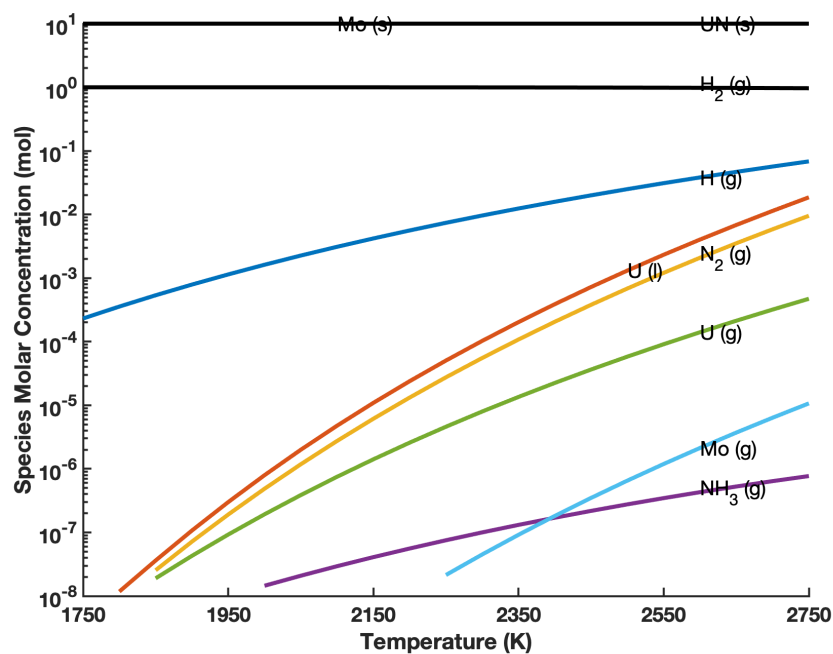


Figure 3.3: Predicted thermodynamic stability of UN in hydrogen with primary corrosion product species. Gibbs free energy minimization calculations were performed using 10 mole UN and 1 mole H_2 reactants at a pressure of 1 atm for temperatures of 1750- 2750 K

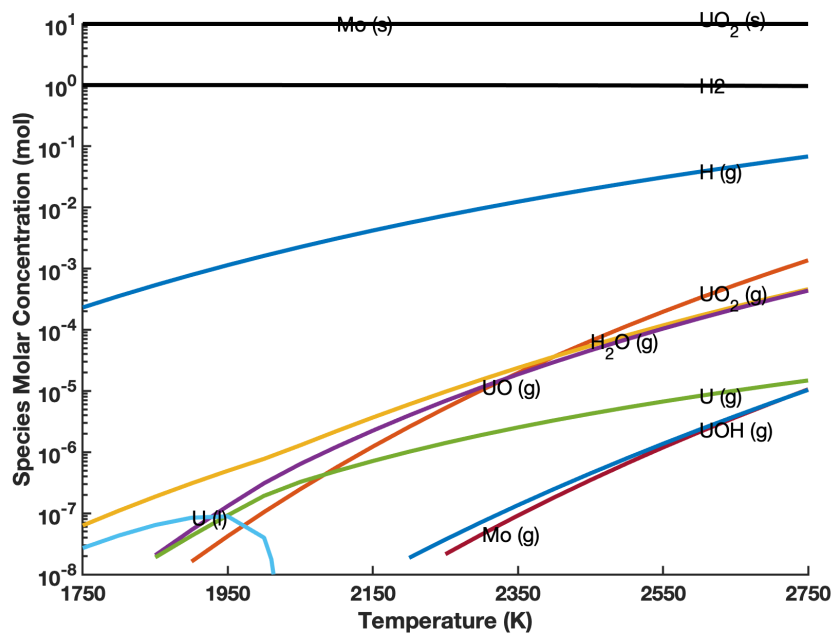


Figure 3.4: Equivalent plot for UO_2 with the same conditions

Chapter 4

Experimental Description

4.1 Sample Fabrication

For stock Mo samples, the Mo used was an arc-cast composition obtained from H.C. Stark. The 2 cm diameter rod was cut via electro discharge machining (EDM) to thicknesses of 5 mm and subsequently into quartered wedges. The cut surfaces of the samples were ground down with SiC papers to remove *sim* 100 μm of material including any Cu contamination from the EDM. They were then polished to $\sim 15\ \mu\text{m}$ size.

Mo-cermet samples were produced at NASA Marshall Space Flight Center using a powder blending method originally designed for W-cermets [96] which I performed for the powders used in this study. Yttria-stabilized zirconia (ZrO_2) particles are used as a surrogate for UO_2 fuel. The YSZ in this experiment came in the form of microspheres from Cospheric with a specified diameter range of 212–250 μm . The vendor reported composition is summarized in Table 4.1. This is equivalent to 5.7 mol% $\text{YO}_{1.5}$ which leads to a partially stabilized tetragonal crystal structure[97]. Small 5–7 μm Mo powder was mixed with (212–250 μm diameter YSZ spheres along with a polyethylene binder. From previous testing with W-cermets it is known that highly angular powders produce less desirable sintered microstructures. Mo powders from two different vendors were imaged with SEM as shown in Figure 4.1 and the powder with more acceptable sphericity was chosen. Ceramic volume loadings of 40, 50, 60, and 70 vol% were investigated in this study. Corresponding quantities of Mo powders and YSZ particles were weighed and measured in batches. For each batch,

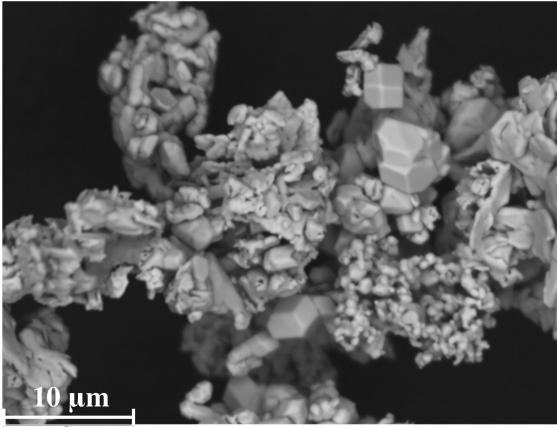
approximately 0.5 weight percent (wt%) milled Honeywell AC617A polyethylene binder was added and the mixture was shaken in a Turbula shaker-mixer for an hour. Subsequently, the mixture was removed from the Turbula and heated in a beaker on a hot plate to above the drop point of the organic binder (170 °C). Once heated, a magnetic stir bar was used to stir the mixture and bond the Mo-powders onto the larger YSZ particles. The mixture was removed from heat and allowed to cool once no uncoated zirconia particles could be visually identified (10 minutes).

Blended and coated powders were consolidated into subscale cermet sample coupons using spark plasma sintering (SPS). Prior to sintering, approximately 13 g of the Mo-ZrO₂ mixture was transferred to a 20 mm diameter graphite die and punch set and lined with grafoil. This assembly was loaded into a direct current sintering (DCS-15) furnace housed at NASA Marshall Space Flight Center. SPS utilizes an electric current which is conducted through the graphite punch and die to resistively heat powders to temperature. Mo-cermets coupons were produced using temperatures of 1400-1600 °C with dwell times of 5–10 minutes and 50 MPa applied pressure. Typical temperature and pressure ramp rates were 100 °C and 10 MPa per minute respectively. Other work optimized these production values at 1400 °C and 5 min dwell time for Mo-cermets [98]. The sintering was performed by Kelsa Benensky.

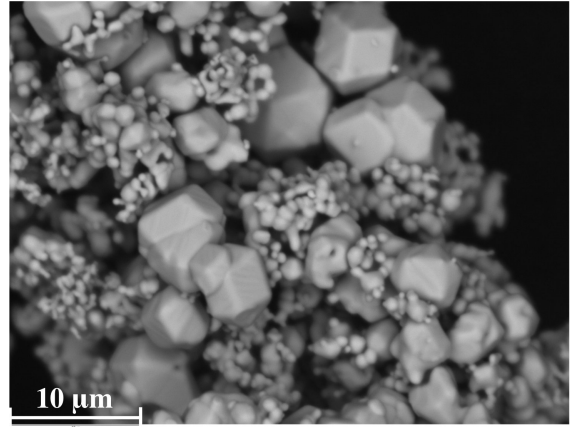
Prior to testing, samples were ground flat with silicon carbide paper until the grafoil and carbide reaction layer on the top and bottom faces was removed ($\sim 150\text{ }\mu\text{m}$ thickness). Samples were sectioned into quarter-moon geometries using a diamond saw and polished to 5 μm finish. After polishing, samples were cleaned with deionized water, degassed in acetone, dried, measured, and weighed using a precision balance. Typical sample initial mass was $\sim 2.5\text{ g}$. Example images of prepared samples are shown in Figure 4.3. Sample preparation and polishing was performed both at NASA Marshall and at UTK in SERF.

Table 4.1: YSZ Composition Information

Compound	wt%
ZrO ₂	94.5
Y ₂ O ₃	5.1
Al ₂ O ₃	0.25
Fe ₂ O ₃	< 0.002
Na ₂ O	< 0.005

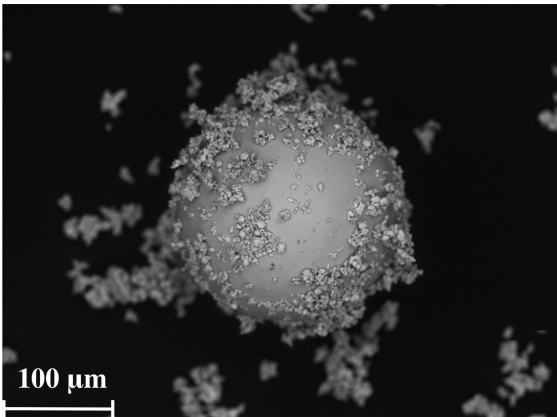


(a) Highly angular Mo powders

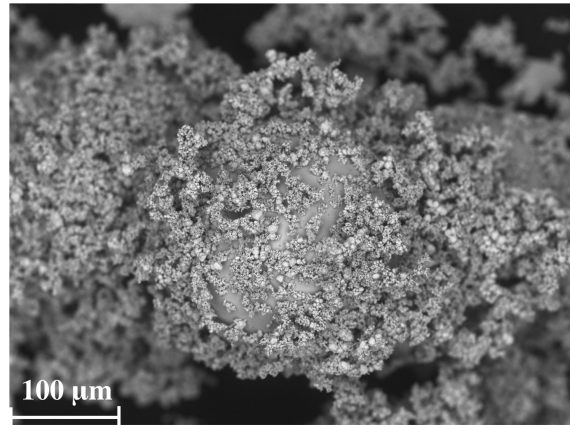


(b) Mo powder with acceptable sphericity

Figure 4.1: Powders with better sphericity resulted in more uniform sample coatings. Angular powders resulted in poor bonding to YSZ particles. Imaged by Ms. Ellen Rabenberg at NASA Marshall

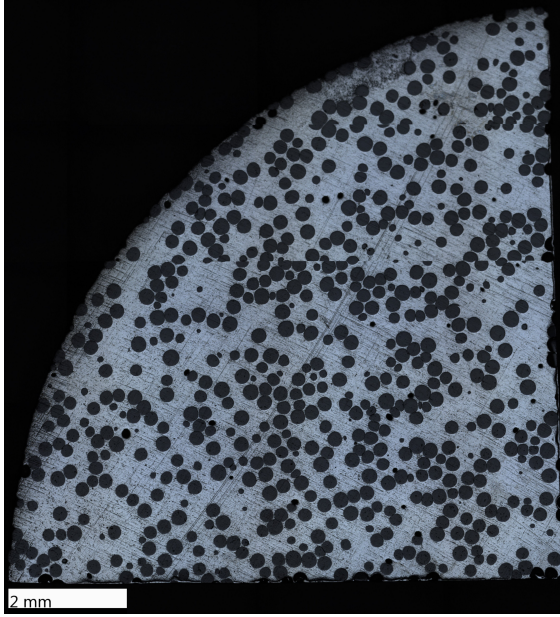


(a) Poor Coating

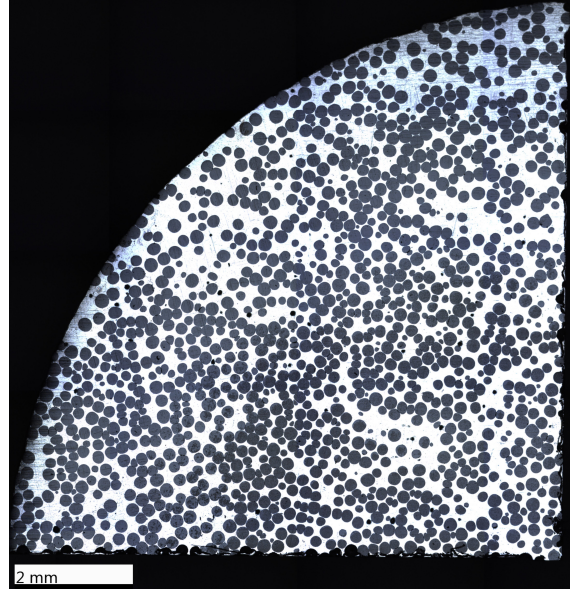


(b) Uniform Coating

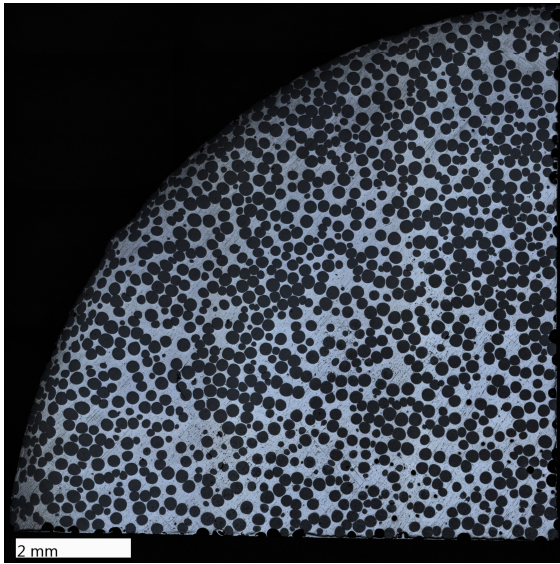
Figure 4.2: Example of Mo-coated YSZ particles using the powder-coating process with a Honeywell AC617A polyethylene binder. Imaged by Ms. Ellen Rabenberg at NASA Marshall



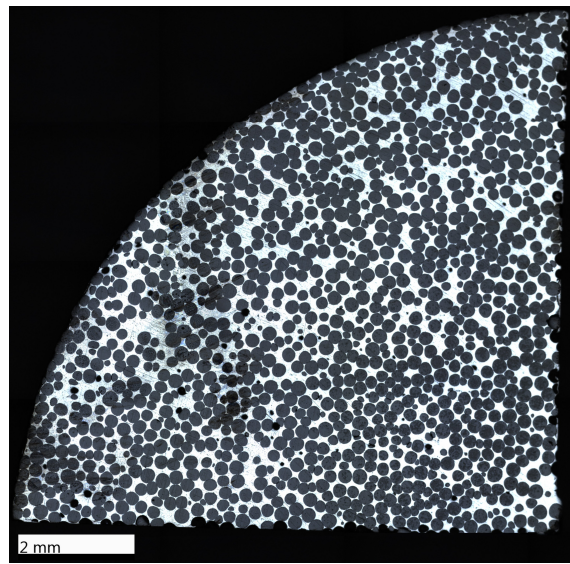
(a) 40 vol% YSZ loading



(b) 50 vol% YSZ loading



(c) 60 vol% YSZ loading



(d) 70 vol% YSZ loading

Figure 4.3: As fabricated microstructure of Mo-YSZ cermets with 40, 50, 60, and 70 % volume loadings prior to final polishing

4.2 Experimental Setup

4.2.1 CFEET

The first furnace used for high temperature testing in hydrogen was located at NASA Marshall Space Flight Center, the Compact Fuel Element Environmental Test (CFEET) facility. CFEET is a furnace designed specifically to test candidate fuels for the NASA NTP program. The CFEET facility is designed to test subscale samples up to 4 in. long with a 1 in. diameter to maximum operating temperatures up to ~ 2700 K in flowing hydrogen. The operating H_2 pressure is 1 atm with flow rates of 500-1000 standard cubic centimeters per minute; these are both much lower than that of a full scale NTP system. Figure 4.4 shows the exterior of the CFEET vacuum chamber and Figure 4.5 highlights the internal CFEET components.

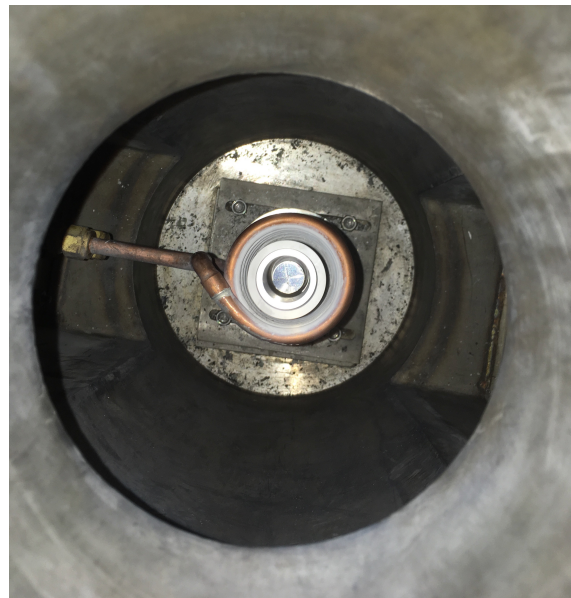
Samples are heated using a copper coil with a SP-16 50 kW power supply at 45 kHz. The sample holder area is within a BN insulator which protects the W susceptor. The W is inductively coupled to the coil which is resistively heated. Both the insulator and the susceptor are cylinders that are open at the top allowing the sample to be view through the top viewport of the vacuum chamber. They also have a midline window to observe the side of the sample. The system uses two different 2-color pyrometers to give temperature readings, a Williamson Pro 80 and Ircon Modline 5R. The manufacture's report the valid temperature range for the Williamson as 600-2800 °C with accuracy of $\pm 0.25\text{-}0.5\% + 2.0$ °C, with the Ircon temperature range of 1000-2500 °C and accuracy of $\pm 0.5\% + 2.0$ °C. The pyrometers were calibrated by viewing the melting of Nb, Zr, and Hf. The Ircon is mounted above the vacuum chamber looking down through the top viewport and records the temperature at the samples top face. The Williamson views through a side viewport between a hole in both the susceptor and insulator and is used as the reference to set operational power and maintain the desired set temperature. Inside the susceptor, a W rod was used to hold up a 2 cm diameter pure Mo sample plate. This plate was chosen to be compatible with the Mo-cermets. Samples are then placed on this Mo plate during testing. Figure 4.6 (modified from Benensky [28]) shows a schematic of the CFEET interior including the sample position and the H_2 flow path.



Figure 4.4: The Compact Fuel Element Environmental Test (CFEET) facility at NASA Marshall Space Flight Center



(a) Loaded BN Insulator



(b) CFEET interior prior to test

Figure 4.5: CFEET components with samples in place

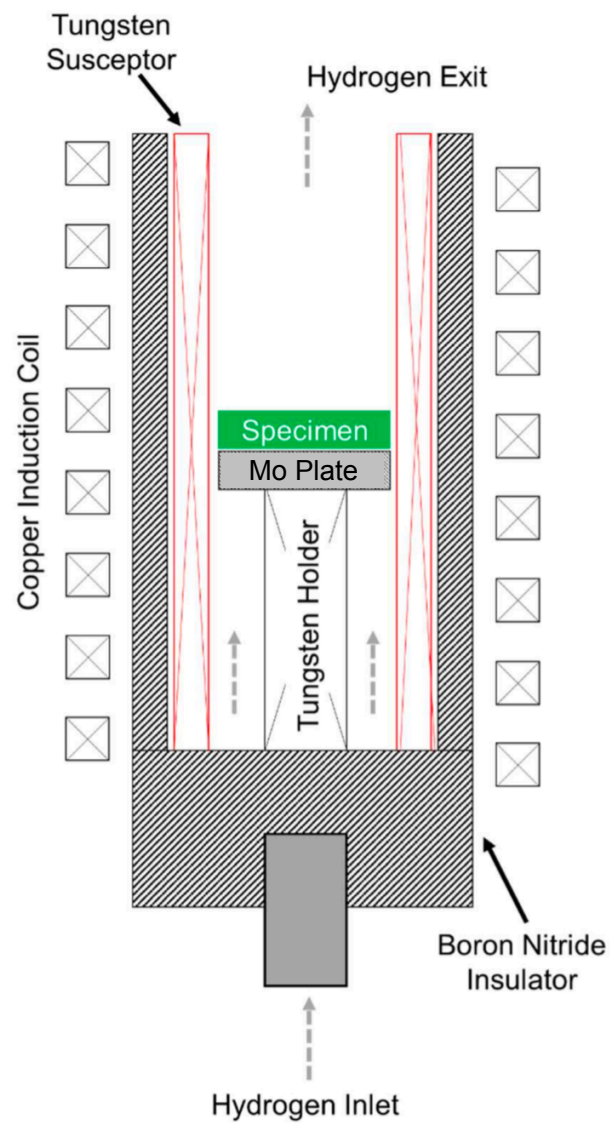


Figure 4.6: Schematic of CFEET interior showing the H_2 flow path. Modified from Benensky [28].

The series of tests performed in this study included both a steady-state test held for 80 min at constant temperature as well as thermal cycling tests, where the test was operated for four cycles of 20 min with cooling to room temperature between each cycle. Examples of these operating condition are plotted in Figure 4.7. The maximum temperature ramp rates were ~ 400 K/min during heating, and ~ 450 K/min during cooling.

In recent work, it has been shown that the corrosion rate for SiC at NTP conditions depends on the hydrogen flow rate [28]. This is a limitation of the small scale testing that can be performed in CFEET and it is important to do further testing at prototypic higher hydrogen pressures and flow rates to fully qualify a NTP fuel form such as in the NTREES facility.

4.2.2 BWXT Furnace

The second round of testing was performed at a hydrogen furnace owned by BWX Technologies (BWXT) in Lynchburg, Va at the Lynchburg Technology Center. This furnace is designed by Centorr Vacuum Industries. The heated area is made of a series of tungsten plates that are separated by an air gap. A diagram of the furnace is shown in Figures 4.8 and 4.9. The furnace supports a hydrogen atmosphere at 15 psi. Samples were introduced and then the chamber was evacuated and subsequently purged with argon (Ar) for 60 min. Following the Ar purge, H₂ was introduced for 60 min prior to beginning heating. Flow was controlled by the exiting hydrogen, when the pressure dropped below 15 psi H₂ would be reintroduced at a flow rate of 9 L/min for 15-18 seconds. This frequency for reintroducing H₂ was only able to be observed prior to heating and not throughout the entire run. At the beginning of the H₂ purge the cycle time was 135 sec while after an hour of purge the cycle was 77 sec. The observed average H₂ flow rates were calculated to be 1.0-2.1 L/min. The temperature ramp rate was 50 K/min for both heating and controlled cooling of the furnace. There was a <5 min hold at 1873 K where temperature control shifted from a thermocouple to the pyrometer. This hold period caused a 100 K drop in temperature during the heating ramp and a similar heating spike during the controlled cooling ramp. Once the test temperature was reached the samples were held for 80 min before the controlled cooling step. Below 350 K the cooling was no longer controlled and an Ar purge was started for 60

min while the furnace cooled to room temperature. The achieved test temperatures were 2200 K, 2430 K and 2630 K as measured by the Ircon SR-35C15 pyrometer sighted on the sample. A representative temperature ramp is shown in Figure 4.10

4.3 Analysis Techniques

4.3.1 Microscopy

Optical and scanning electron microscopy (SEM) have been used to characterize these Mo-cermet samples both before and after testing. The Keyence VHX optical microscope at NASA Marshall was used to image samples prior to thermal cycling and to monitor sample evolution between thermal cycles. A Zeiss optical microscope was used to create stitched full surface images of the samples. The SEM microscope at UTK's Joint Institute for Advanced Materials (JIAM) is a Zeiss EVO. Advantages of electron microscopy include high resolution, creating images with topographic contrast using secondary electrons, and the ability to get elemental information based on backscattered electrons. SEM can be coupled with an x-ray detector to give Energy Dispersive X-ray Spectroscopy (EDS) measurements which give local elemental composition.

4.3.2 FIB

A Zeiss Auriga Focused Ion Beam (FIB) microscope located at UTK at the JIAM facility was used to prepare sample specimens for subsequent transmission electron microscopy (TEM). A focused ion beam microscope typically has both a scanning electron beam for imaging and a gallium ion beam to mill or cut small lamella out of a sample material. Sample preparation involves depositing a layer of platinum to protect the surface of the material and then using the ion beam to gradually cut out a desired section about 10–15 μm in length and 10 μm deep. This lamella is attached to a grid to allow for thinning and subsequent TEM viewing. Once attached to the grid, the ion beam is used to gradually remove material from a targeted window until the sample is about 100 nm in thickness. This is an appropriate thickness for viewing in the TEM.

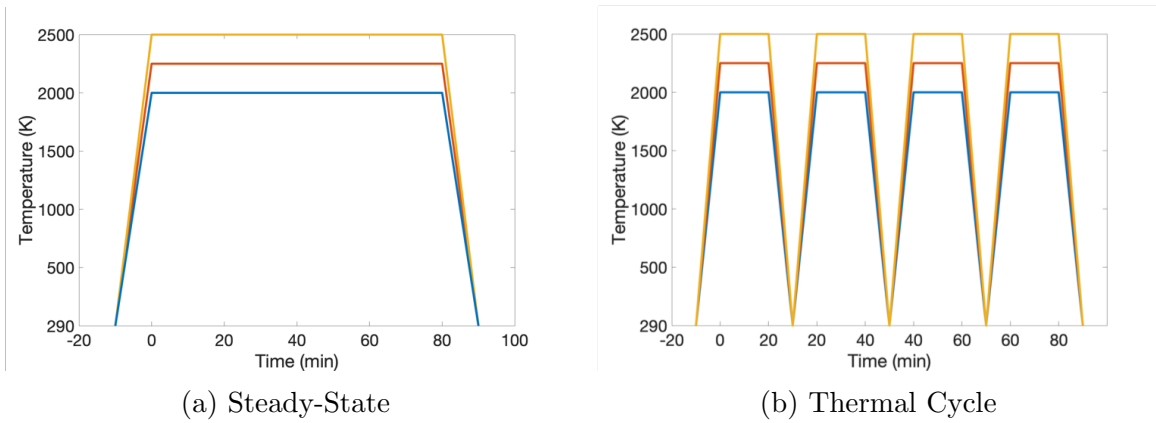


Figure 4.7: Example of the a) steady-state and b) thermal cycling high temperature exposures performed at CFET.



Figure 4.8: BWXT Hydrogen Furnace Exterior - BWX Technologies Inc. Lynchburg Technology Center – Refractory Metal Hydrogen Furnace

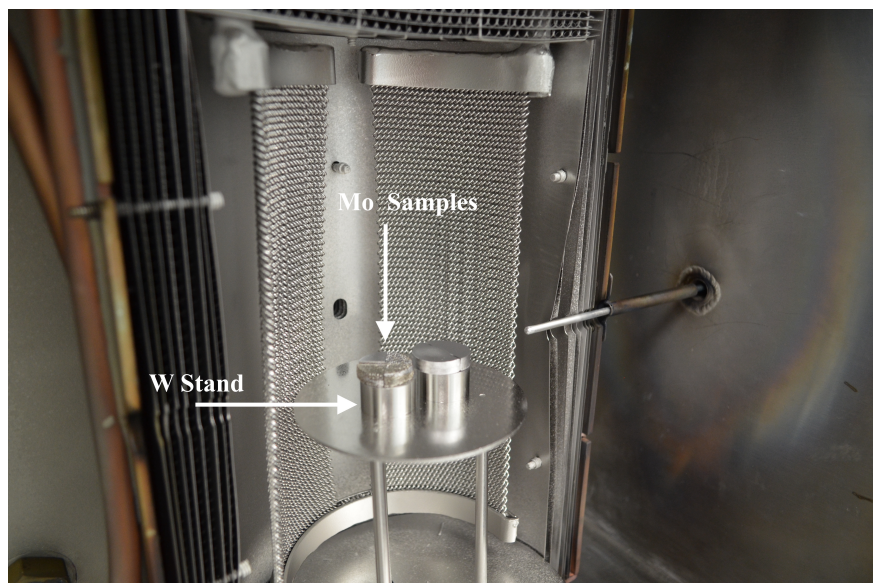


Figure 4.9: BWXT Hydrogen Furnace Interior BWX Technologies Inc. Lynchburg Technology Center – Refractory Metal Hydrogen Furnace Interior

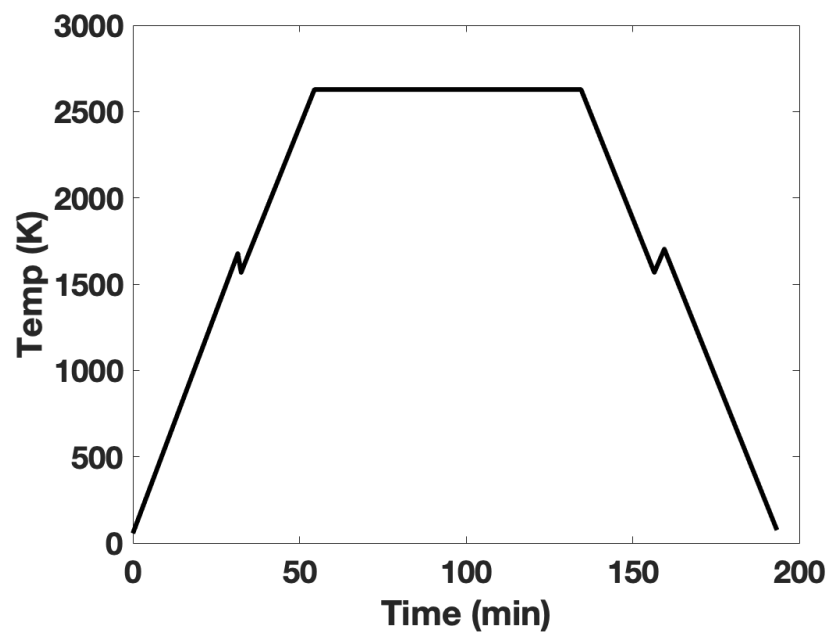


Figure 4.10: Representative temperature profile inside the BWXT furnace

4.3.3 TEM

Transmission electron microscopy is a useful tool to view nanometer sized features in a given microstructure. A Zeiss Libra 200 MC TEM at UTK at the JIAM facility was used to investigate the boundary between the zirconia particles and the Mo matrix after hot hydrogen testing. In contrast to an SEM where secondary or backscattered electrons are collected on the same side of the sample as the electron beam, TEM transmits the electron beam through the entire sample thickness. This can allow for imaging at a much higher resolution on the nanometer scale. It also allows for the collection of diffraction patterns based on the crystal structure of the sample region. This diffraction pattern can be used to give information about the lattice spacing which may be modified locally by stress concentration.

4.3.4 X-ray Diffraction

X-ray diffraction (XRD) is a useful technique to characterize the phase of a bulk sample. The x-ray diffractometer used in this study is an Empyrean located at the JIAM facility. The fundamentals of x-ray diffraction are exploiting Bragg's Law which describes how x-rays will have constructive interference at a given angle based on the characteristic spacing of the crystal lattice of a solid material. When this condition is not met, there is destructive interference and no peak is observed. By surveying a wide range of angles, a spectrum can be produced to and compared to a reference sample for phase identification.

4.3.5 Raman Spectroscopy

Raman spectroscopy is a very useful characterization technique that probes the vibrational, rotational and low-frequency modes of a system. Raman spectroscopy takes advantage of the inelastic scattering of a monochromatic light source incident on a sample. There are several competing effects of the incident light on the sample, including Rayleigh scattering, Raman scattering, fluorescence, absorption and transmission. Raman scattering occurs when the incident beam inelastically scatters off of the electron cloud. This is a direct interaction with the electric field of the monochromatic light that induces a dipole moment based on the polarizability of the molecule. The process is described as exciting an electron to a

virtual energy state but it is not a real transition between energy levels. Since the normal Raman scattering process only requires a virtual energy state, a specifically tuned wavelength of incident light is unnecessary. However, if the wavelength of the light is tuned to a real energy level, then a resonance effect is observed which increases the probability of interaction dramatically. The Raman effect is very small compared to Rayleigh scattering and so a filter must be used to block the elastically scattered light and detect the fainter Raman signal. The energy change in the detected light from Raman can be both redshifted (Stokes) or blue shifted (Anti-Stokes) based off if the excited electron was initially in a ground or excited rovibrational state. As the ground states have a higher probability of being populated, the Stokes scattering has a higher intensity than the Anti-Stokes scattering. Raman scattering can only be induced if the polarization of the molecule will change. This means that for a vibrational mode to be Raman active that there needs to be a net change in the electron cloud position around the molecule. This is comparable to the need for a change in dipole moment in infrared absorption spectroscopy. However, the Raman effect can occur in nonpolar molecules which makes it different from and complementary to IR absorption spectroscopy. Like many other techniques, Raman data is often compared to a standard spectrum and used like a fingerprint to identify chemical constituents. The setup for acquiring a Raman spectrum requires a laser source, focusing lenses, a filter to block Rayleigh light, a high-resolution spectrometer and a detector. The laser light for a typical Raman analysis is in the visible range. Different wavelengths may be chosen to avoid fluorescence, impart less laser damage to the sample or be in resonance. Raman is useful technique for characterizing ceramics and so is useful to view the zirconia in these samples. Raman cannot be use to characterize metals however.

Pomfret et al. investigated the structural and compositional characterization of yttria-stabilized zirconia (YSZ) using Raman spectroscopy [83]. . Without the yttria, ZrO_2 is monoclinic and only adopts a cubic phase above 2400°C . Figure 4.11 shows the Raman spectrum of 8% YSZ and highlights the low frequency structure that corresponds to the phonon structure of cubic YSZ. The most dominant Raman band is at 617 cm^{-1} and is “assigned to a triply degenerate F_{2g} mode associated with pairs of oxygen atoms in the crystal lattice moving out of phase with one another.”[83] With increasing yttria content

within the cubic phase, they noted that the dominant Raman peak shifted from 617 to 598 cm^{-1} which corresponds to an increase in the lattice parameter of 5.143 to 5.152 Å. They also produced samples with monoclinic and tetragonal structures in addition to the cubic phase when yttria content was below 8%.

YSZ samples were then exposed to a 5% H_2 in Ar environment for 6 hours at 1000°C. Figure 4.12 illustrates the 50% depression in the Raman intensity following this treatment with no significant shift in peak location. They noted that the change is stable over time and also reversible if exposed to air at 1000°C to reoxidize the sample. This change was even repeated in cycling the same sample through these conditions repeatedly. As peak positions were stable, there is no change to the lattice parameter or percent yttria. This result was also confirmed by XRD measurements. The researchers conclude that the loss of intensity is caused by a change to surface polarizability as a result of reducing species at the surface by increasing the concentration of metal cations relative to oxide ions. They conclude that because of no change in the XRD pattern that this must be a surface effect. They also performed X-ray photoelectron spectroscopy (XPS) measurements that suggest that a reduced form of zirconia is present on the surface and is stable in both air and humidity.

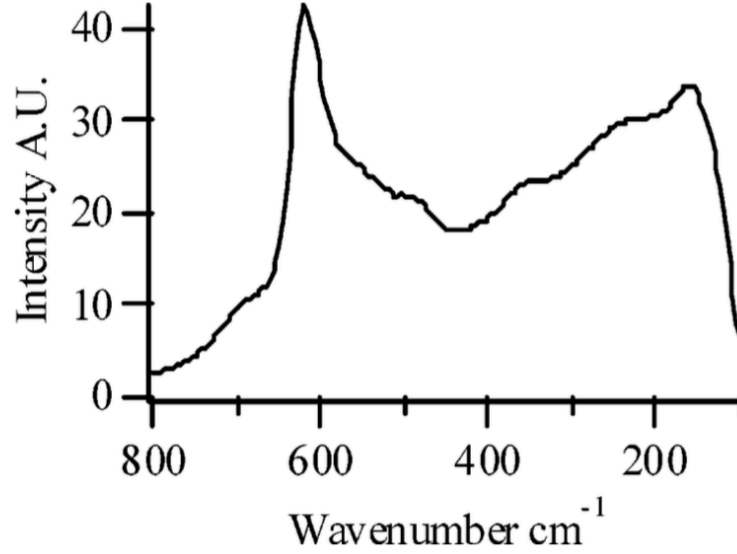


Figure 4.11: Stokes Raman spectrum of YSZ. The band structure from 100 to 800 cm^{-1} is characteristic of the cubic YSZ phonon modes. The bands at higher frequencies are attributed to sample fluorescence caused by the 1064-nm laser. [83]

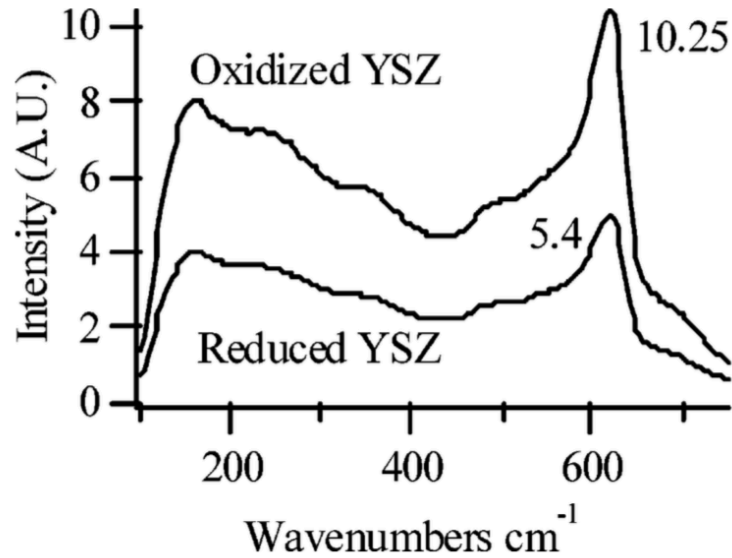


Figure 4.12: The effect of a reducing atmosphere on YSZ Raman signal intensity. Exposure to a reducing environment at high-temperature precipitates a drop in Raman signal intensity of 25-50% compared to oxidized sample. Peak structure and position is unchanged, indicating no change in the chemical composition of the bulk crystal structure. [83]

Chapter 5

Results and Discussion

5.1 Pure Molybdenum Results

5.1.1 Mass Loss

Figure 5.1 displays the mass loss for the pure Mo samples tested in the BWXT furnace. The measured mass loss is divided by surface area of the sample directly exposed to the flowing H, i.e., the upper face and the curved circumferential edge (1.5 cm^2). These areas were derived by using an average radius (based on 30 measurements for quartered samples). Error bars include propagation of the error in these radius measurements through the area formulas as well as the uncertainty from the mass measurements. As the density of Mo is 10.28 g/cm^3 the values for mass loss in mg/cm^2 are essentially equivalent to an assumed uniform depth change in μm .

The mass loss at 2200 K is at the resolution limit of the balance used (0.1 mg). One sample showed mass increase following the test (0.4 mg), however it had a small amount of bonding to a neighboring sample which showed mass loss of 0.2 mg. It is likely that the transfer of material from the bonding and slight imprecision in measurement account for the observed weight gain.

An estimate of the mass loss due to vapor pressure alone was performed using the Langmuir equation for free evaporation in a vacuum [99] where dm/dt is the rate of mass loss per unit area, p the vapor pressure, M the molecular weight of the effusing vapor, R the

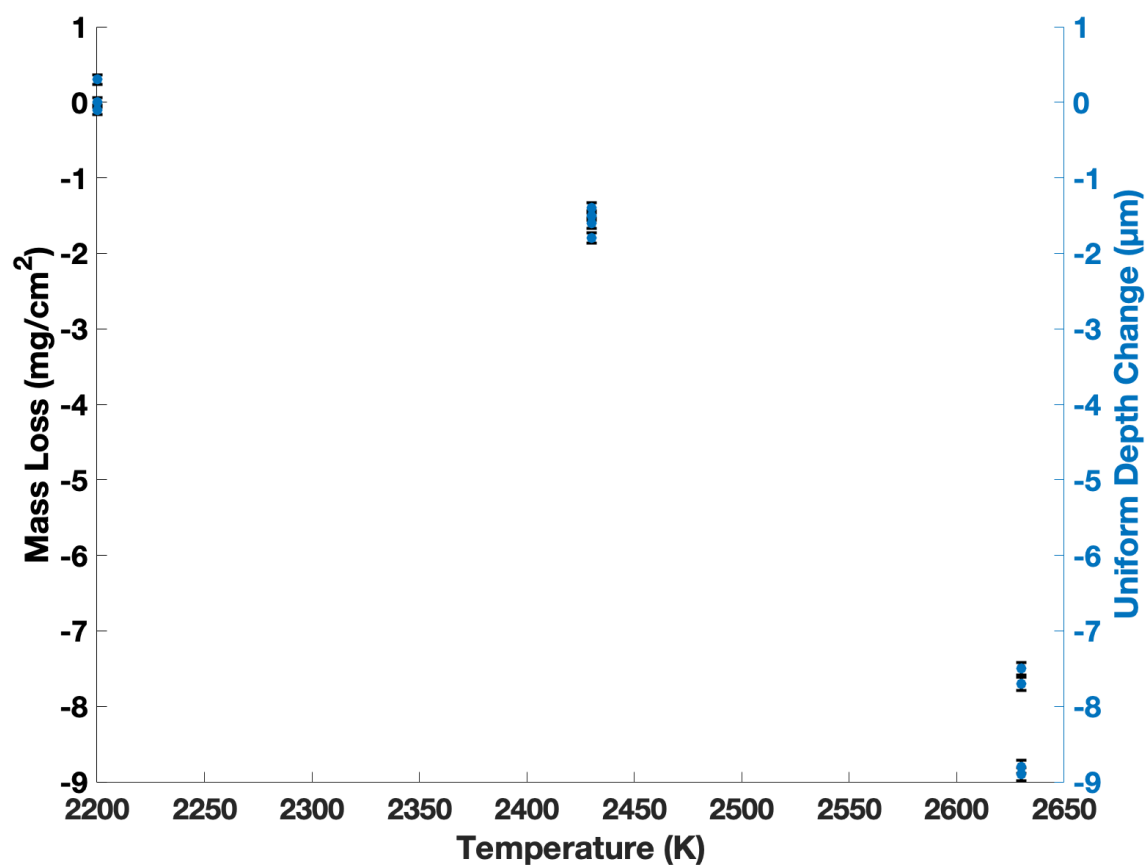


Figure 5.1: Mass loss for Mo samples exposed to high temperature H_2

gas constant, T the absolute temperature and r as a way to quantify potential reflection. [100] In a vacuum $r=0$ is used.[101]

$$\frac{-dm}{dt} = (1 - r) p \sqrt{\frac{M}{2\pi RT}} \quad (5.1)$$

Vacuum vapor pressure values are calculated from the provided equation in the CRC handbook [102] for Mo. Figure 5.2 shows this Mo loss rate calculated for an 80 min exposure and the experimental mass loss on a log scale vs inverse temperature with the zero and mass gains neglected at 2200 K.

The averaged experimental mass loss data are generally very close to the values predicted from vapor pressure sublimation at 2200 and 2430 K. However, at 2630 K the average experimental value was 8.2 mg/cm², whereas the mass loss predicted from vapor pressure is higher by 40% (4.3 mg/cm²). Experimental results can often have lower vaporization rates than those calculated for a variety of factors including oxide present on the surface or due to moderate vapor shielding as the experiment is performed in 1 atm of H₂ and not under vacuum. [103] Static inert atmospheres (e.g. He, Ar, N₂) decrease the vaporization of metals as transport away from the surface is limited in the boundary layer and this is disturbed only by the natural circulation in the inert atmosphere [56], [70]. For molybdenum at 1 atm this reduction can be 2–3 orders of magnitude lower than values predicted by vapor pressure[104]. As the observed values are close to those predicted by vapor pressure loss, the modest flow rate must be increasing them back up to the vacuum derived values. As the flow in the BWXT furnace is pulsed and not constant, the erosion may be occurring primarily during the time when the gas is pulsed in and be relatively low when the gas is more static.

5.1.2 Grain Size

The grain size of the tested samples was observed at the surface from thermal etching of the grain boundaries; the average grain diameters are shown in Figure 5.3a. All test temperatures are significantly above the recrystallization temperature for pure Mo (1253–1323 K for 1 h [105]). Other studies have shown that static grain growth is stronger for arc melted Mo than for powder metallurgy Mo [106]. At the highest temperature, some of the grains at

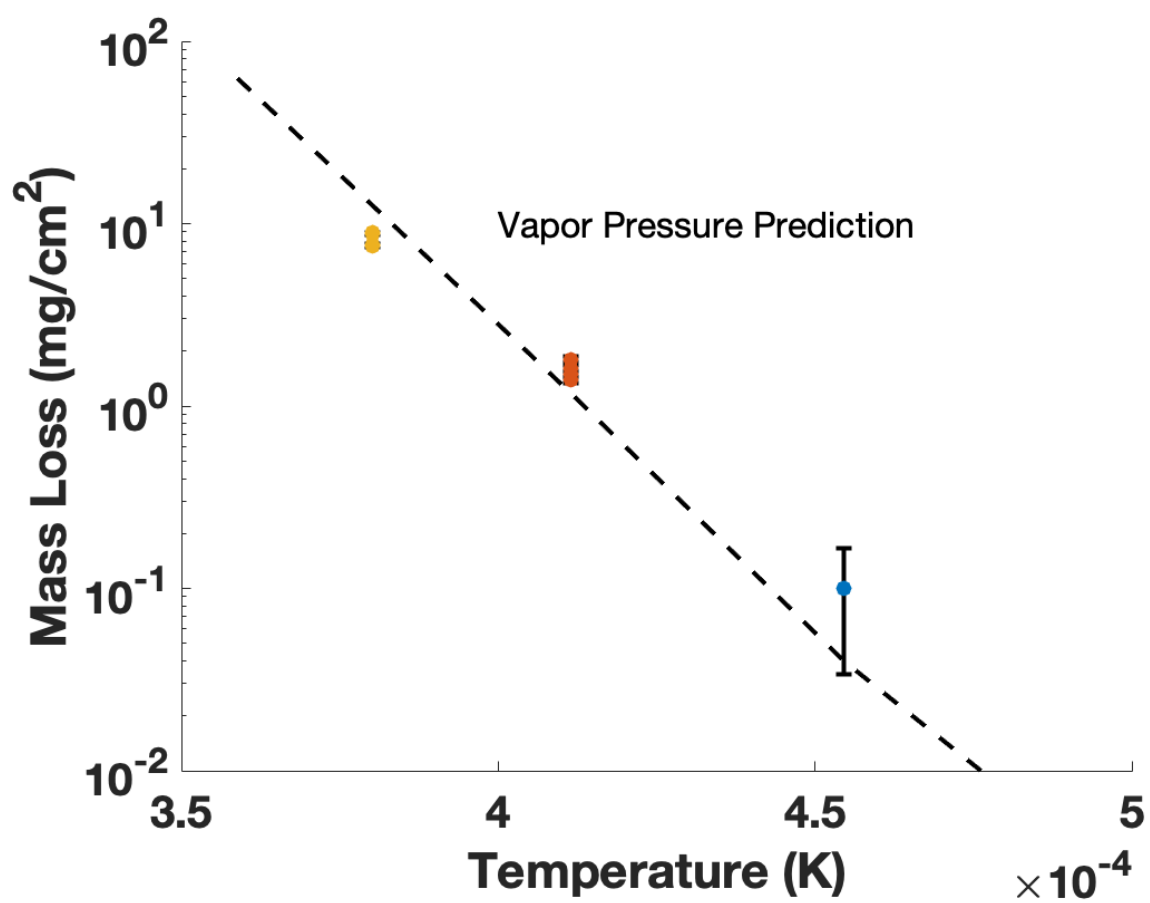


Figure 5.2: Mo vapor pressure loss calculated vs observed

the surface had sizes up to 5 mm, which was also the thickness of the samples. The general grain growth equation with an Arrhenius relationship is shown in equation 5.2 where d is the grain size at given exposure time, d_0 is the initial grain size, t is time, k_0 is a constant, Q is the activation energy, R is the gas constant and T is absolute temperature.

$$d^2 - d_0^2 = tk = tk_0 \exp\left(\frac{-Q}{RT}\right) \quad (5.2)$$

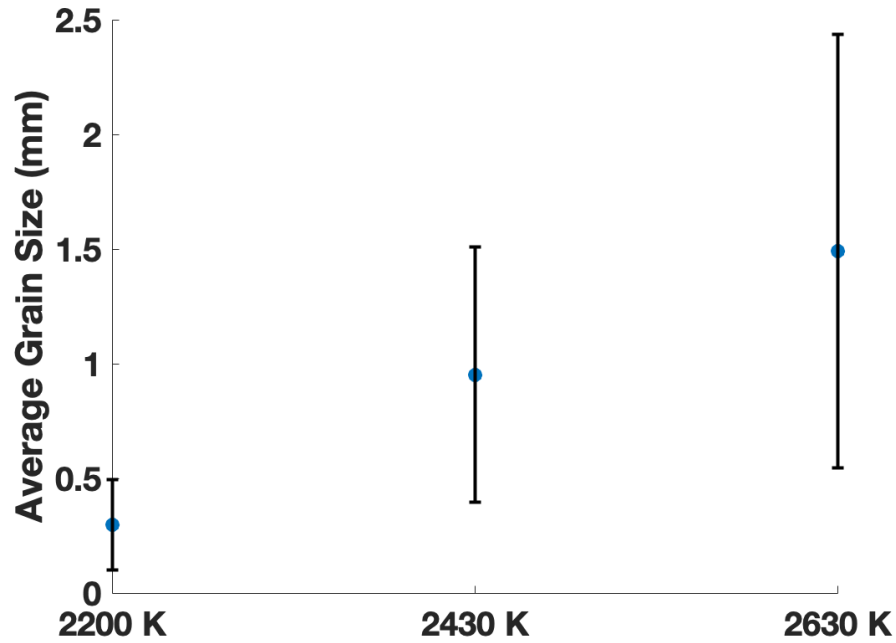
Figure 5.3b plots the $\ln(d^2 - d_0^2)$ against $1000/T$ to derive the grain growth activation energy $Q = 160$ kJ/mol.

5.1.3 Microstructure

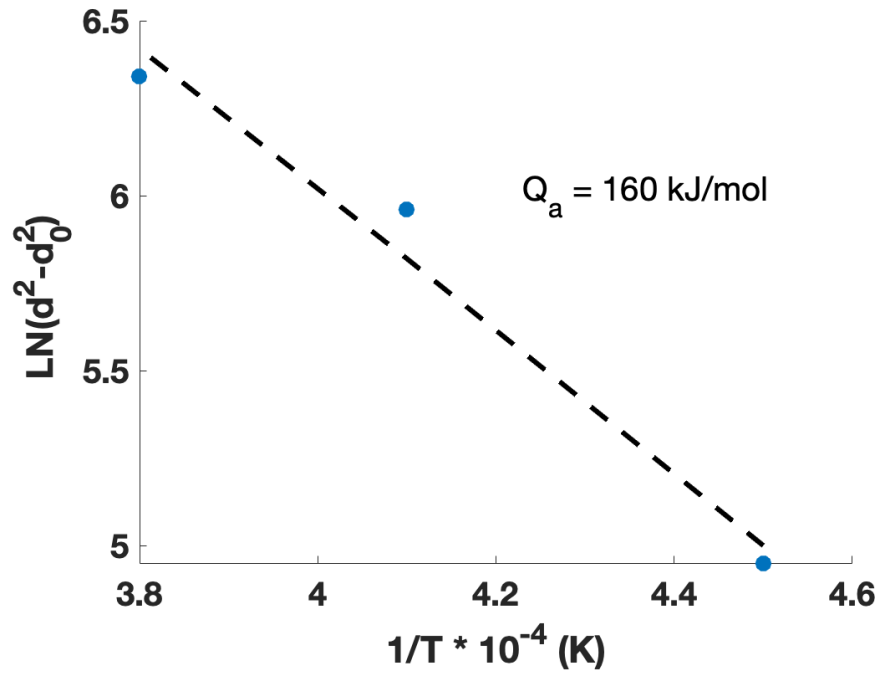
Figure 5.4 displays full size images of samples a) as prepared, b) at 2200 K, c) at 2430 K, d) at 2630 K. Figure 5.5 displays a typical Mo sample surface from the 2630 K exposure. Particularly in the highest temperature test the sample surface has considerable contamination from ZrO_2 deposits as verified by EDS and Raman spectroscopy that originate from the YSZ in the adjoining cermet samples tested at the same time.

Figure 5.5 also shows surface indentations or erosion with a wave like appearance. These occur on both the surface and the bottom of the specimen in contact with the W stand. The appearance of these ridged features is reminiscent of the residual outline of subgrains that no longer exist following the 80-minute exposure. The new grain boundaries are clearly visible and can pass through these wave-like indentations without causing any pattern interruption.

At high magnification an interesting fine-scale striated pattern was visible. These striations are essentially parallel within a single grain, with some minor directional shifts frequently observed near grain boundaries. Neighboring grains have a different directional orientation for the striations as is shown in Figure 6a. These striations were visible in all tested samples but were the most pronounced at the highest test temperature (2630 K). The spacing between these ledges are typically 100-200 nm. They continue in essentially the same direction throughout the grain, with some waves/bends if the surface is deformed. They can also shift in angle as the ledges approach the grain boundary as is shown in Figure 6c. Additionally, there are some areas where a plateau region is visible as highlighted

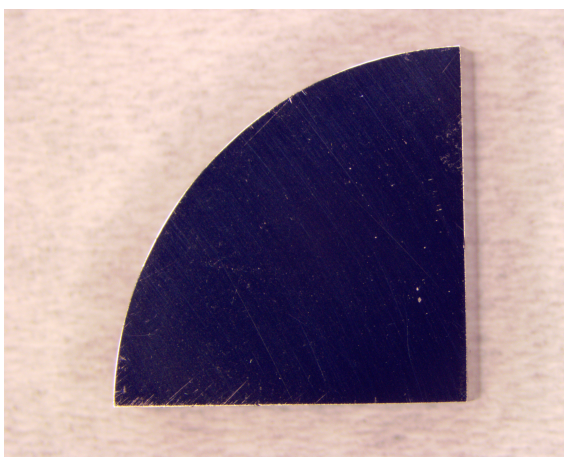


(a) Mo average grain size with test temperature. Initial size $\sim 3 \mu\text{m}$.

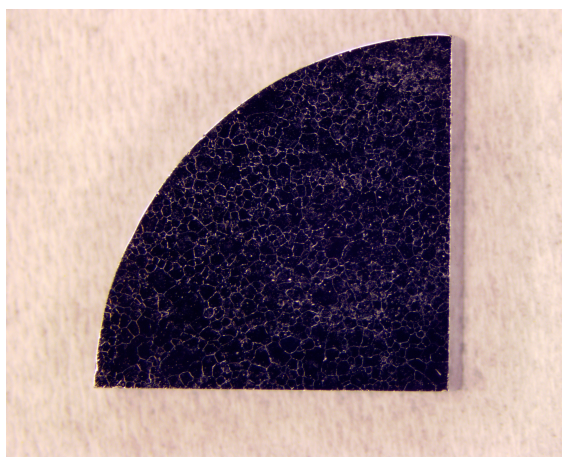


(b) Mo grain size activation energy regression

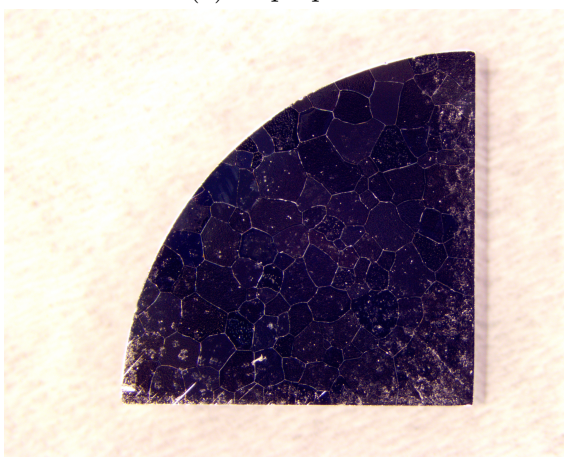
Figure 5.3: Mo grain size



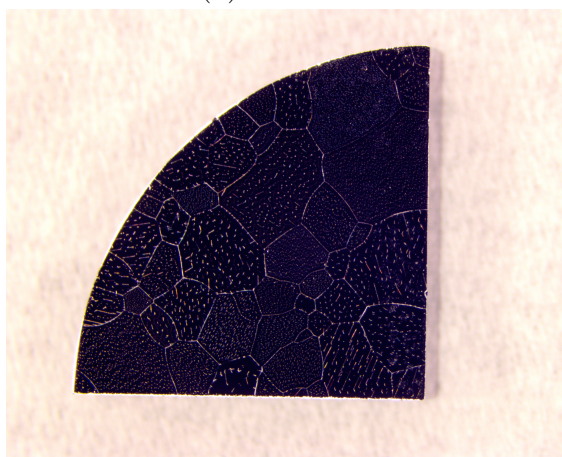
(a) as prepared



(b) at 2200 K



(c) at 2430 K



(d) at 2630 K

Figure 5.4: Mo samples as prepared and tested

in Figure 6d. This image was taken at the edge of the sample and the slightly rounded edge from polishing may have acted as the initiation site for the plateau type behavior. This phenomenon is postulated to be due to the formation of monoatomic ledges during evaporation and subsequent pileup of ledges leading to observable microscopic features.

The terrace-ledge-kink theory[107] has been used to analyze surface ledges that appear during crystal growth at high temperatures. This same theory of monoatomic ledges applies to the evaporation of metals [108], [109]. For example, observations of ledges at microscopic scale have been observed in [111] copper after electropolishing [110]. Microscopic scale ledges were also observed in both deposition and sublimation of HgI_2 [111]. The ledges are formed by bunching of atomic steps during evaporation or dissolution. These prior studies indicate that the rate of evaporation may be important in whether these steps form. For example, an increase in current density caused the ledges to not appear in copper during electropolishing[110]. There can also be threshold step spacings (50-70 nm in copper) beyond which steps are too far apart to interact and form ledges. Smooth areas can be present where the threshold step spacing is exceeded. Hirth and Pound provide dynamics for monatomic ledges for a variety of metals with characteristic spacings and cite $\lambda_0 = 192$ nm for Mo at 2700 K along [110] planes [109].

The ledges appear to align with three different types of crystallographic planes as evaluated by correlating grain images with the EBSD data for that grain. The most common observation (50% of grains) is that the ledge direction aligns with a [100] direction in the crystal easily visualized as the elevated edge of a cube such as in Figure 7a. The atoms may be removed along either a $\{100\}$ or $\{110\}$ type plane to match this direction. Another set of ledges can be seen with perpendicular $\{110\}$ planes. These were much smaller in height than the first case and had different spacing (e.g., 100-150 nm in one direction vs 300-400 in the perpendicular direction). An example of this behavior is shown in Figure 7b and 7c. The final type aligns to a [210] direction and corresponds with some of the tallest ledges with heights as tall as ~ 100 nm. The alignment of this behavior likely depends on where the monoatomic ledges were initiated e.g grain boundaries, screw dislocations and other uneven surface features such as the rounded edge near the observed plateaus in Figure 5.6d. Hirth

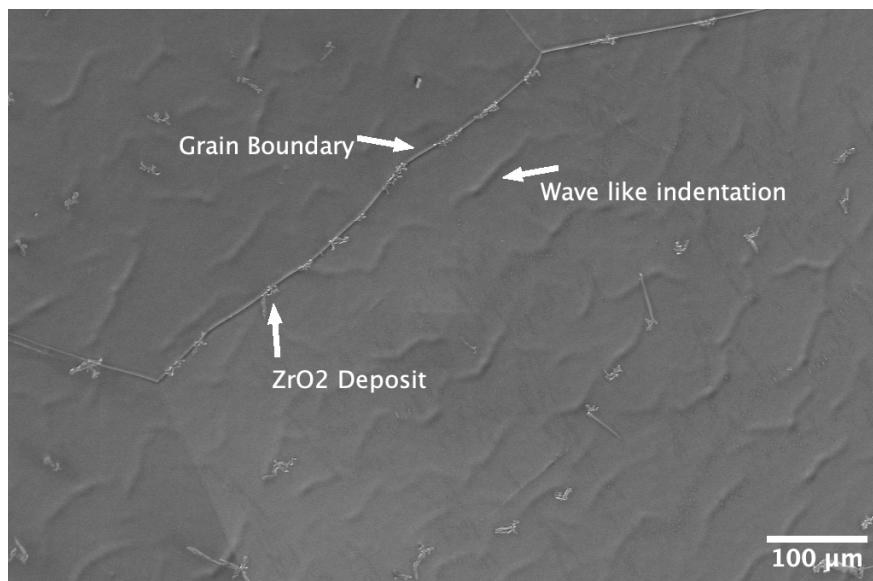
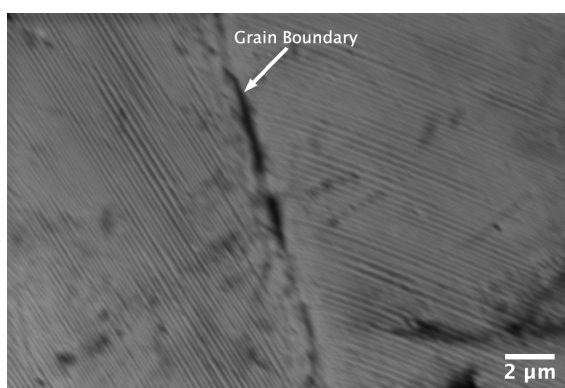
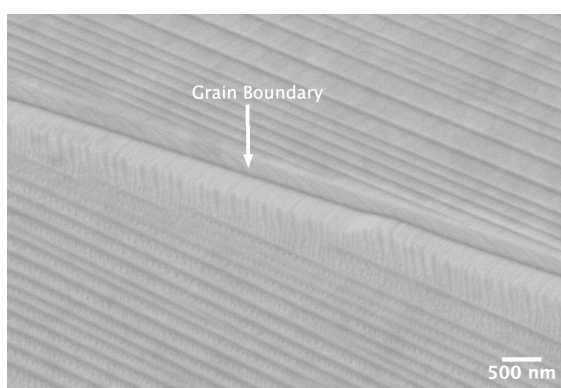


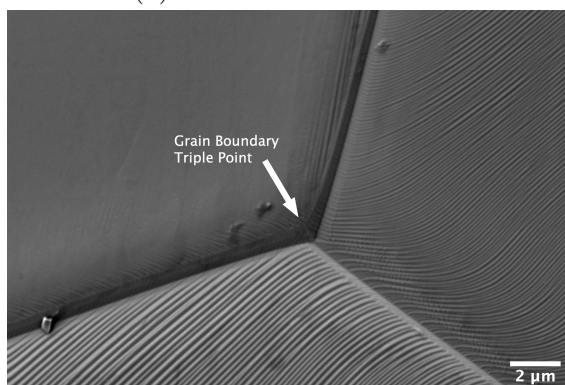
Figure 5.5: Secondary electron image of Mo surface highlighting the visible grain boundaries, ZrO_2 deposits and the wave like indentations. Sample tested at 2630 K in H_2



(a) different orientations



(b) similar orientations



(c) Ledge curvature near grain boundary intersection



(d) Plateaus in the Mo near the edge of the sample surface

Figure 5.6: Ledges in Mo grains at 2630 K

suggests bcc monoatomic ledges form on $\{100\}$ and $\{110\}$ planes[109]. Common bcc slip plane directions $\{110\}$ and $\{211\}$ [112], [113] also may be relevant.

At the highest temperatures (2430 and 2630 K) two of the four tested samples had visible deformation along the bottom of edge of the Mo sample. If the entire sample was not resting on the W stand, a rim of differing height was visible. When measuring with calipers the height difference was around 10–20 μm where the area in contact with the stand was lower than the rim that was hanging over the edge. It is difficult to explain this deformation/thermal creep as there was no applied stress beyond the slight gravitational load of the specimen mass. An image of the bottom surface is shown in Figure 5.9 and shows the visual difference from the top face. The surface features on the bottom face did not exhibit any apparent crystallographic dependence; these features extended across grain boundaries without interruption as shown in Fig. 5.9. The rim height difference and enhanced waviness could suggest there was local melting of the Mo where the sample was in contact with the W stand. EDS did not show a distinguishably higher amount of W in the contact region. The wave-like indentations in the Mo shown on the surface in Figure 5.5 are even more pronounced on the bottom of these samples where it had contact with the stand.

5.2 Cermet results

5.2.1 Pre-Test Characterization

The Mo-YSZ cermet samples were produced by SPS at 1400 °C for 10 min at 50 MPa with YSZ volume loadings ranging from 40–70%. The YSZ particles are $\sim 200\text{ }\mu\text{m}$ in diameter. Following grinding and polishing these samples were imaged with SEM as shown in Figures 5.10–5.12. The density of these samples is high compared to the theoretical density (TD) based on the volume loading, with most exceeding 98% TD. Overall there is rather good spacing of the YSZ particles considering the powder blending method used to produce the samples. Usually there is at least a thin layer of Mo between adjacent particle. No cracks are found in the Mo matrix and very little evidence of porosity observed during polishing. The interfacial bond between the YSZ particles and the Mo matrix appears robust.

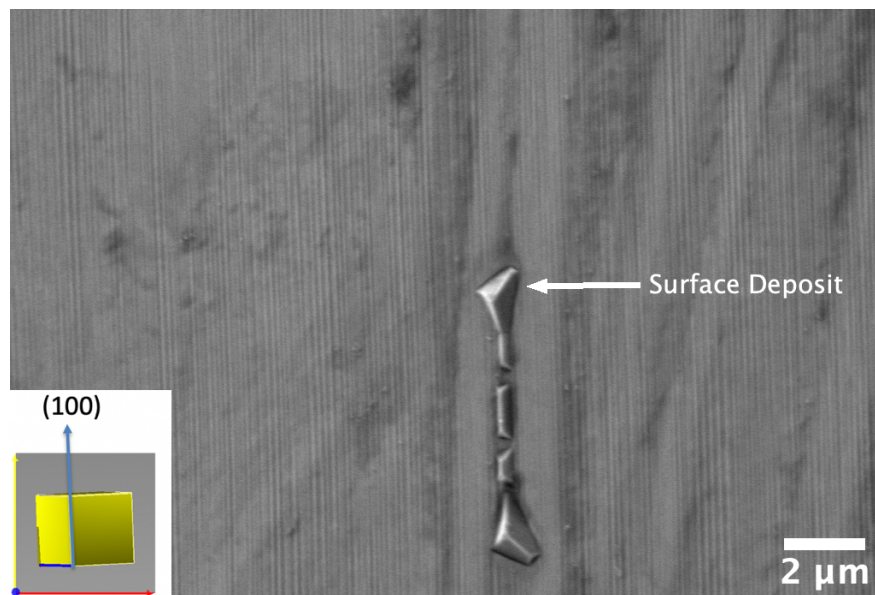
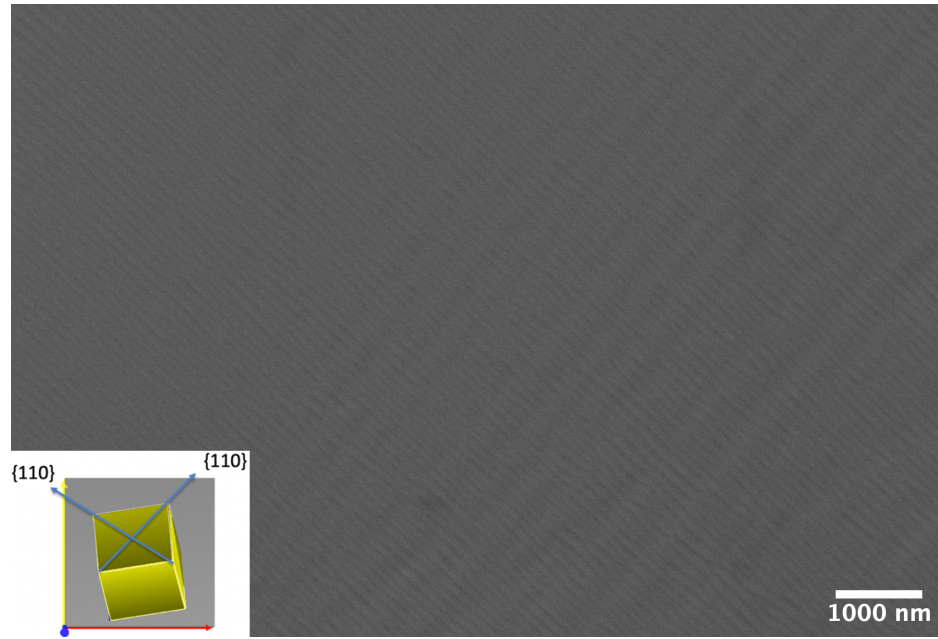
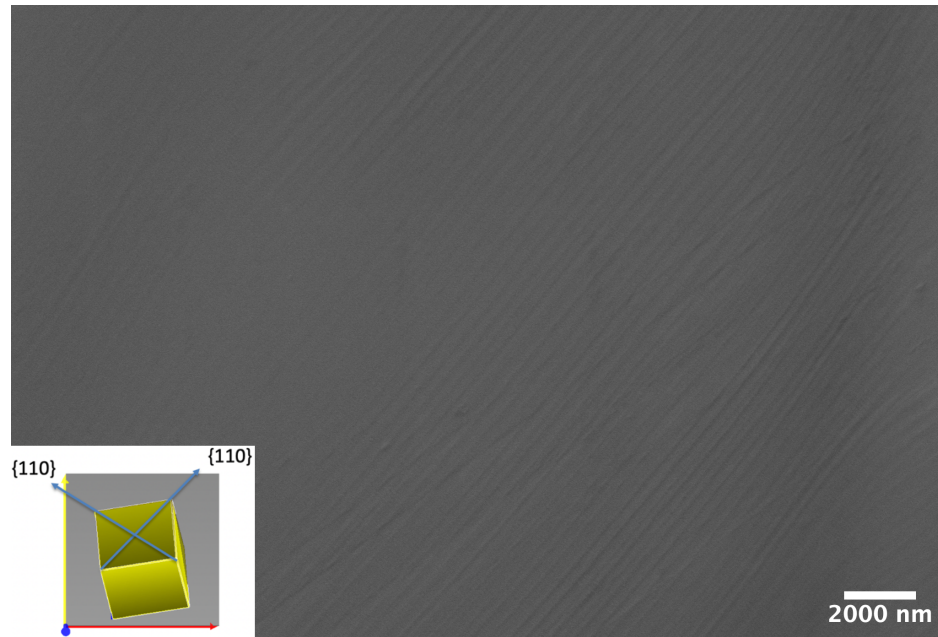


Figure 5.7: Orientation example for striations matching a (100) direction with an orientation cube as an insert

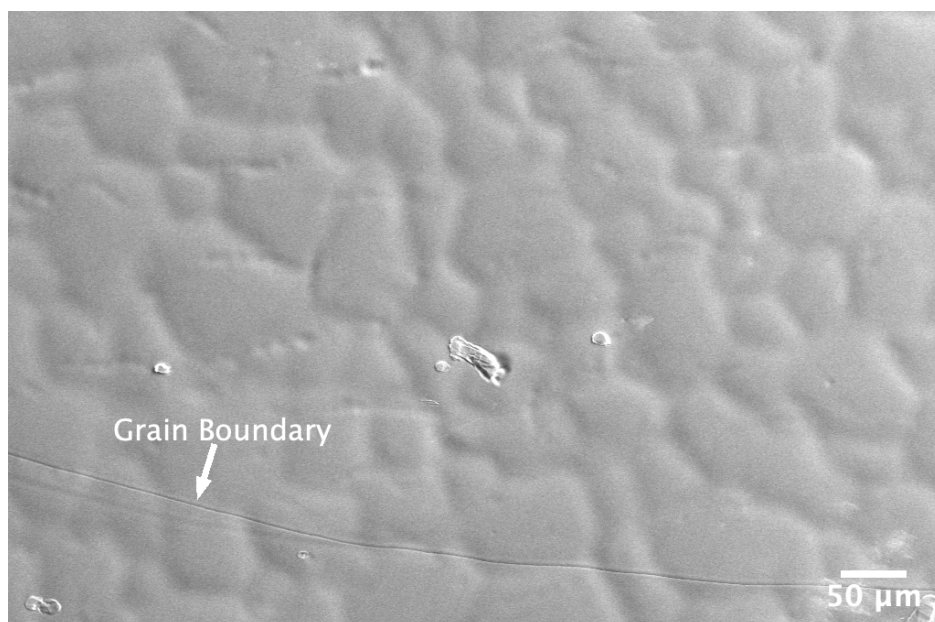


(a) 10kx

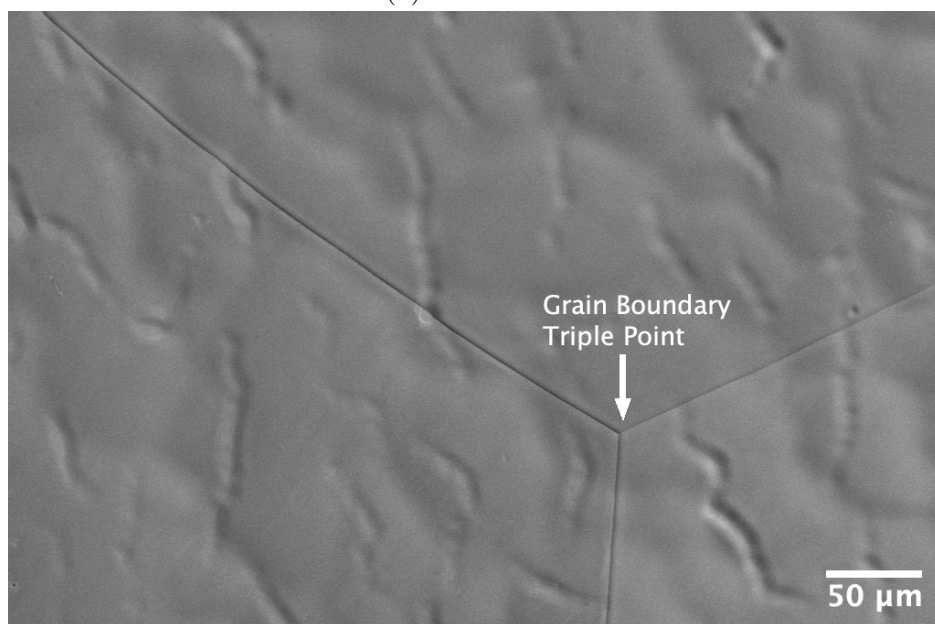


(b) 5kx

Figure 5.8: Orientation example for striations matching 2 $\{110\}$ planes in the same grain with the orientation cube as an insert. Taken at different focus and magnification to show both directions of ledges



(a) Location 1



(b) Location 2

Figure 5.9: Waviness on bottom surface of Mo tested at 2630 K. Appearance is similar to eroded grains, however the real grain boundary is clearly visible and passes through the wavy indentations

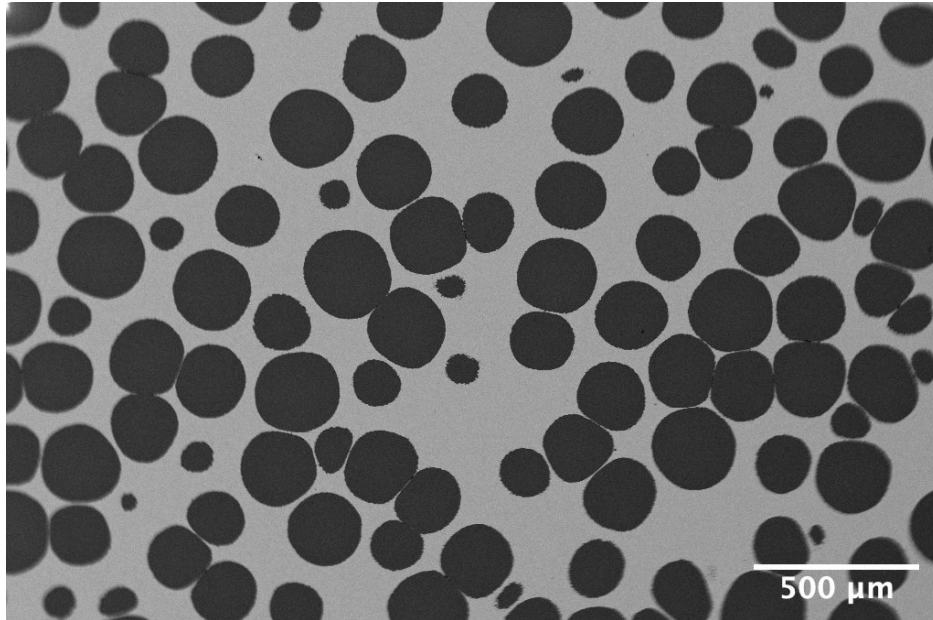


Figure 5.10: 60 vol % cermet prior to testing

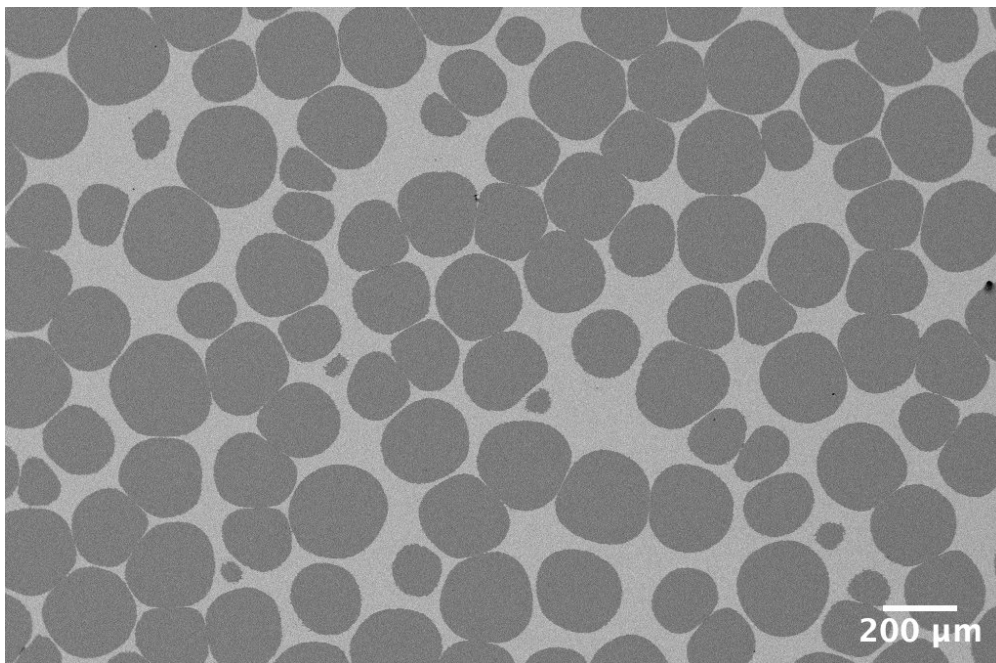


Figure 5.11: 70 vol % cermet prior to testing

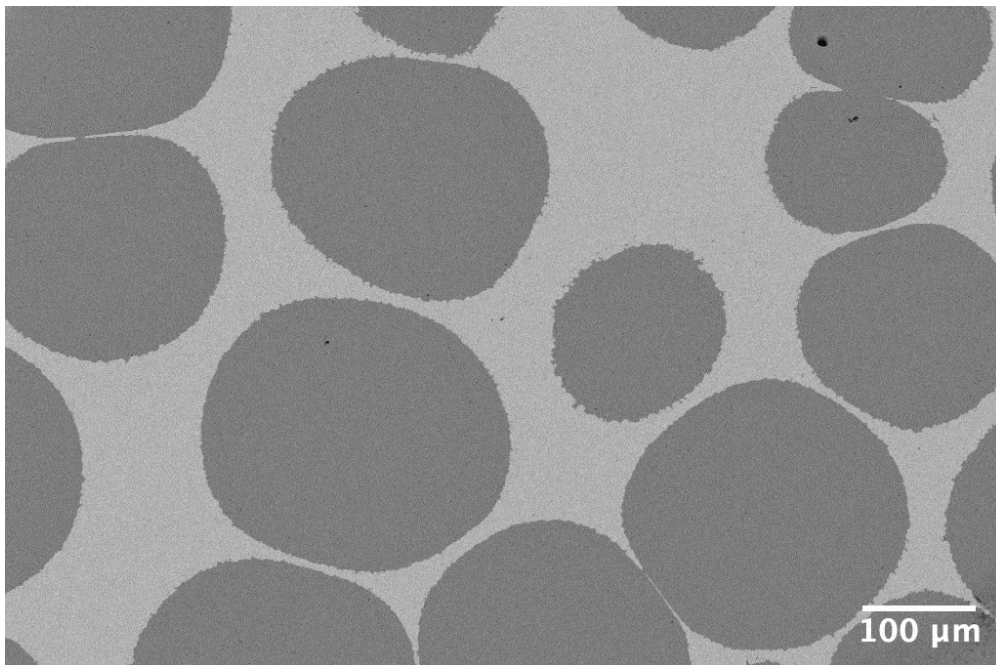


Figure 5.12: Close up of 70 vol % cermet prior to testing

5.2.2 Mass Loss

Sample mass loss after high temperature exposure to hydrogen is a primary metric for assessing the performance of a NTP fuel form. Mass loss data was normalized to surface area exposed to the hydrogen, which includes the top surface and circumferential edge but not interior edges or bottom surface. Mass loss data of these unclad samples provides an upper bound of the mass loss for a worst case scenario where the exterior permeation barrier cladding or coating of the reactor core is breached during operation or after multiple thermal cycles when hydrogen has penetrated through the cladding as described by Baker [43]. Mass loss behavior obtained from the hydrogen exposures in the CFEET and BWXT facility is displayed in Figures 5.13 with steady-state tests shifted for better readability. The plot also includes an approximate uniform corrosion depth change axis that was calculated by multiplying the mass loss by the theoretical density of a 50 vol% cermet (this approximation assumes mass loss is equal in the Mo and YSZ, which is unlikely, and that all mass is lost from the surface). The mass data for the 40 vol% thermal cycled (TC) sample at 2500 K was only obtained following the first thermal cycle, as the sample fused to the testing plate in subsequent cycles which prevented the collection of accurate mass data. The steady-state (SS) tests at 2000 K were conducted on roughly four times as much material as all subsequent tests and with different sample geometry, but the surface area normalization provides comparable data.

It is evident from Figure 5.13 that the mass loss increased with increasing exposure temperature and increased YSZ content. The maximum mass loss in the CFEET tests (12 mg/cm^2) was experienced by the 70 vol% YSZ sample thermal cycled at 2500 K. This corresponds to a uniform surface recession of $\sim 15 \text{ }\mu\text{m}$, which is considered to be an acceptable amount of corrosion during the mission lifetime and represents a loss of less than 0.7 wt%. The maximum mass loss for the BWXT tests (17.5 mg/cm^2) was from the 50 vol% YSZ sample at steady-state. This seems anomalous; both the 50% and 70% steady-state samples at 2630 K had slightly greater mass loss than the thermal cycled series.

It is noteworthy that the mass loss for all tested samples and test temperatures over the four thermal cycles is sublinear, with the highest rate of change occurring in the first

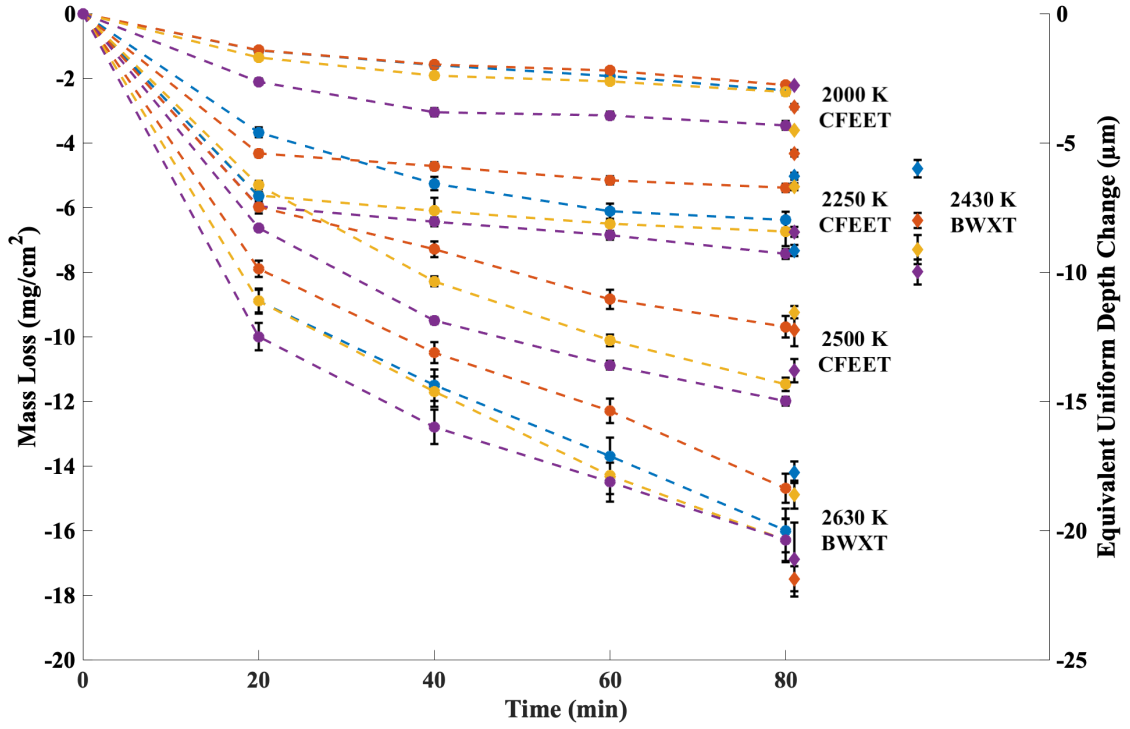


Figure 5.13: Mass loss data in CFEET and BWXT furnaces as a function of testing time for both steady-state (SS) and thermally cycled (TC) Mo-YSZ cermet samples containing 40–70% YSZ particles. SS test (diamonds) were tested for 80 min and are shifted to the right for improved readability

thermal cycle. The reduced mass loss rate for subsequent thermal cycles is particularly dramatic in the low temperature tests. The relatively high mass loss rate in the first cycle may include a small amount loss due any remaining grafoil or molybdenum carbide (present from SPS sintering) from the sample circumferential edge that was not removed during sample preparation.

Historic cermet testing also noted the highest mass loss occurred in the first few minutes of testing; this was attributed to preferential vaporization at the surface of the samples[31]. Unlike other forms of corrosion such as oxidation, a protective surface film does not form that could passivate the corrosion in the H₂ environment. It is evident from Figure 5.13 that the mass loss increases with increasing H exposure temperature. If the mass loss rate is defined linearly excluding the zero point (i.e., fitting a straight line through the 20–80 minute exposure data points) then the average mass loss rate (regardless of volume loading) changes from $\sim 1 \frac{mg}{cm^2 hr}$ at 2000 K and 2250 K to $\sim 5 \frac{mg}{cm^2 hr}$ at 2500 K and $\sim 6.2 - 7 \frac{mg}{cm^2 hr}$ at 2630 K. The 70 vol% YSZ case is illustrative, changing from $1.25 \frac{mg}{cm^2 hr}$ at 2000 K, $1.45 \frac{mg}{cm^2 hr}$ at 2250 K, $5.24 \frac{mg}{cm^2 hr}$ at 2500 K and $6.21 \frac{mg}{cm^2 hr}$ at 2630 K. For a given temperature, the initial rate and the thermal cycled mass loss rate were observed to slightly increase with increasing volume loading of YSZ, which is an indication of higher corrosion rates in the YSZ particles compared to the Mo matrix. Other general trends present in the data include greater mass loss at higher temperature (generally the most predominant effect), and moderately greater mass loss in thermally cycled samples than for steady-state. The 50% YSZ sample at 2500 K is notable in that final mass loss in the steady-state and thermally cycled sample were exactly equal. After the first thermal cycle, the 60% 2250 K sample experienced more mass loss than the 60% YSZ sample at 2500K. However, the difference is within 1 standard deviation of the 2250 K mass loss value and the samples follow normal trends afterwards. The 2000 K steady-state 50% and 60% YSZ samples were the only exceptions to the general trend of thermally cycled samples exhibiting higher mass loss compared to the isothermal tested samples.

Based on the increased mass loss with increasing YSZ loading and known chemical interactions between oxides and hydrogen, it can be assumed that the YSZ is the dominant contributor to the measured cermet mass loss (versus the Mo matrix). This effect can be

estimated by the vapor pressure and using the Mo only mass loss values cite Mo paper. An estimate of the mass loss due to vapor pressure alone was performed using the Langmuir equation for free evaporation in a vacuum 5.1

Estimates for vapor pressures from 2000–2500 K were found in Hoch [114] for ZrO_2 , Jacobson[115] for YSZ, Walsh[116] for Y_2O_3 and the CRC handbook[102] for Mo. These mass loss values were scaled by the vaporized chemical species (YO, ZrO, ZrO_2 , O as the largest contributors) to the mole % of that type of material in the sample. Digitizing the reported vapor pressure from old plots is prone to error, but this gives a good order of magnitude of the effect. These vapor pressure values for Mo are displayed in Table 5.1 along with the observed Mo-only mass loss values. For pure Mo exposed in the BWXT furnace the actual mass loss at 2430 K for a 80 min steady-state test was $1.6 \pm 0.2 \frac{\text{mg}}{\text{cm}^2}$ or a linearized rate of $1.2 \pm 0.1 \frac{\text{mg}}{\text{cm}^2 \text{hr}}$. This is very close in magnitude to the calculated rate from the vapor pressure data of $0.9 \frac{\text{mg}}{\text{cm}^2 \text{hr}}$. However static inert atmospheres (e.g. He, Ar, N_2) decrease the vaporization of metals as transport away from the surface is limited in the boundary layer and this is disturbed only by the natural circulation in the inert atmosphere[56], [70]. For molybdenum at 1 atm this reduction can be 2–3 orders of magnitude lower than values predicted by vapor pressure[104].

Table 5.2 shows the calculated YSZ vapor pressure losses, which are likely an overestimate by up to 40% for the flow rates used based on the Mo values, along with both experimental SS and TC values for the Mo-YSZ cermets. Subtracting the experimental mass loss with the observed Mo vapor pressure and the calculated YSZ vapor pressure values gives an estimate for the additional mass loss due to H corrosion effects in YSZ alone from the SS and TC tests.

A power law curve can be fit to the experimental data from the thermal cycled samples as a function of time. An additional linear loss term using the constant mass loss from vapor pressure can also be included. This linear loss term can make good fits for the data at 2500 K, but will not make good fits at 2600 K. Examples of these curves, without the vapor pressure constant term, are shown in Figure 5.14. These power law coefficients range from 0.35–0.53 for the data at 2500 K, indicating that the mass loss due to hydrogen exhibits on the order of $\frac{1}{3}$ or $\frac{1}{2}$ power law time dependence. The power law coefficients have an tighter

Table 5.1: Mo vapor pressure loss calculated vs observed

Temp (K)	Calculated Mo rate $(\frac{mg}{cm^2 hr})$	Calculated Mo 80 min $(\frac{mg}{cm^2})$	Observed SS Mo 80 min $(\frac{mg}{cm^2})$
2430	0.9	1.2	1.6 ± 0.2
2500	2.2	2.9	-
2630	9.4	12.5	8.2 ± 0.7

Table 5.2: YSZ vapor pressure loss and calculated additional H₂ corrosion

Temp (K)	YSZ vol%	Calc. YSZ rate $(\frac{mg}{cm^2 hr})$	Calc. YSZ 80min $(\frac{mg}{cm^2})$	Observed SS Cermet $(\frac{mg}{cm^2})$	Est H ₂ Corrosion SS Cermet $(\frac{mg}{cm^2})$	Observed TC Cermet $(\frac{mg}{cm^2})$	Est H ₂ Corrosion TC Cermet $(\frac{mg}{cm^2})$
2430	40	0.2	0.2	4.8 ± 0.3	3.8	-	-
	50	0.2	0.3	6.4 ± 0.2	5.6	-	-
	60	0.3	0.3	7.3 ± 0.5	6.5	-	-
	70	0.3	0.4	8.0 ± 0.4	7.3	-	-
2500	40	0.6	0.7	7.3 ± 0.2	4.8	-	-
	50	0.7	0.9	9.8 ± 0.5	7.4	9.7 ± 0.3	7.3
	60	0.8	1.1	9.2 ± 0.2	7.0	11.5 ± 0.2	9.2
	70	1.0	1.3	11.1 ± 0.4	8.9	12.0 ± 0.1	9.8
2630	40	2.7	3.6	14.2 ± 0.3	5.7	16.0 ± 0.7	7.5
	50	3.4	4.5	17.5 ± 0.4	8.9	14.7 ± 0.4	6.1
	60	4.1	5.4	14.9 ± 0.4	6.2	16.3 ± 0.6	7.7
	70	4.8	6.3	16.9 ± 1.1	8.1	16.3 ± 0.6	7.5

distribution at 2630 K ranging from 0.35–0.45 with three of the four volume loadings with coefficients between 0.43–0.45.

5.2.3 Cermet Microstructure

Scanning electron microscopy was used to characterize the surface microstructure before and after H exposure. Optical images were also taken both between thermal cycles and following testing. Overall little difference was observed in the surface features of the steady-state versus thermally-cycled samples over the entire investigated temperature range. Typical back-scattered electron (BSE) SEM images for samples tested from 2000–2630 K are shown in Figures 5.15–5.17. There is no evidence for any heterogeneous attack of the Mo matrix for any of the exposures 2000–2630 K. Figure 5.15 shows the typical surface microstructure after exposure at 2000 K 5.15a and 2250 K 5.15b. A crack is visible in the central YSZ particle in Fig. 5.15a that was thermally cycled at 2000 K.; however, since the YSZ grain boundaries are not well defined and the grain size is small, it cannot be determined if this is intergranular or transgranular cracking. Figure 5.15b exhibits cracking in several YSZ particles following steady-state exposure at 2250 K; the observed cracks are predominantly intergranular, with a few transgranular cracks also observed. Well-defined grain boundaries were visible for both the YSZ particles and the Mo matrix for all samples tested above 2250 K (due to thermal and/or H-assisted chemical etching).

Figure 5.16 shows many typical features for the 2500 K samples including apparent surface debonding between the Mo and YSZ, expansion/deposition of some YSZ material beyond the original particle boundaries onto the surface of the adjacent Mo matrix, and occasional YSZ particle cracking. The YSZ outgrowths were identified via Raman spectroscopy to be tetragonal YSZ, identical to the as-fabricated YSZ particle phase. Overall, the Mo matrix microstructure is only slightly modified by this high temperature hydrogen exposure whereas somewhat more pronounced changes occur in the YSZ particles and at the interface between the YSZ particles and the Mo matrix.

Historic cermet hot hydrogen testing of UO_2 -containing particle fuel for NTP applications observed formation of free uranium at grain boundaries after thermal cycling [40], [48]. We have not observed evidence of an equivalent mechanism in the tested YSZ particles such

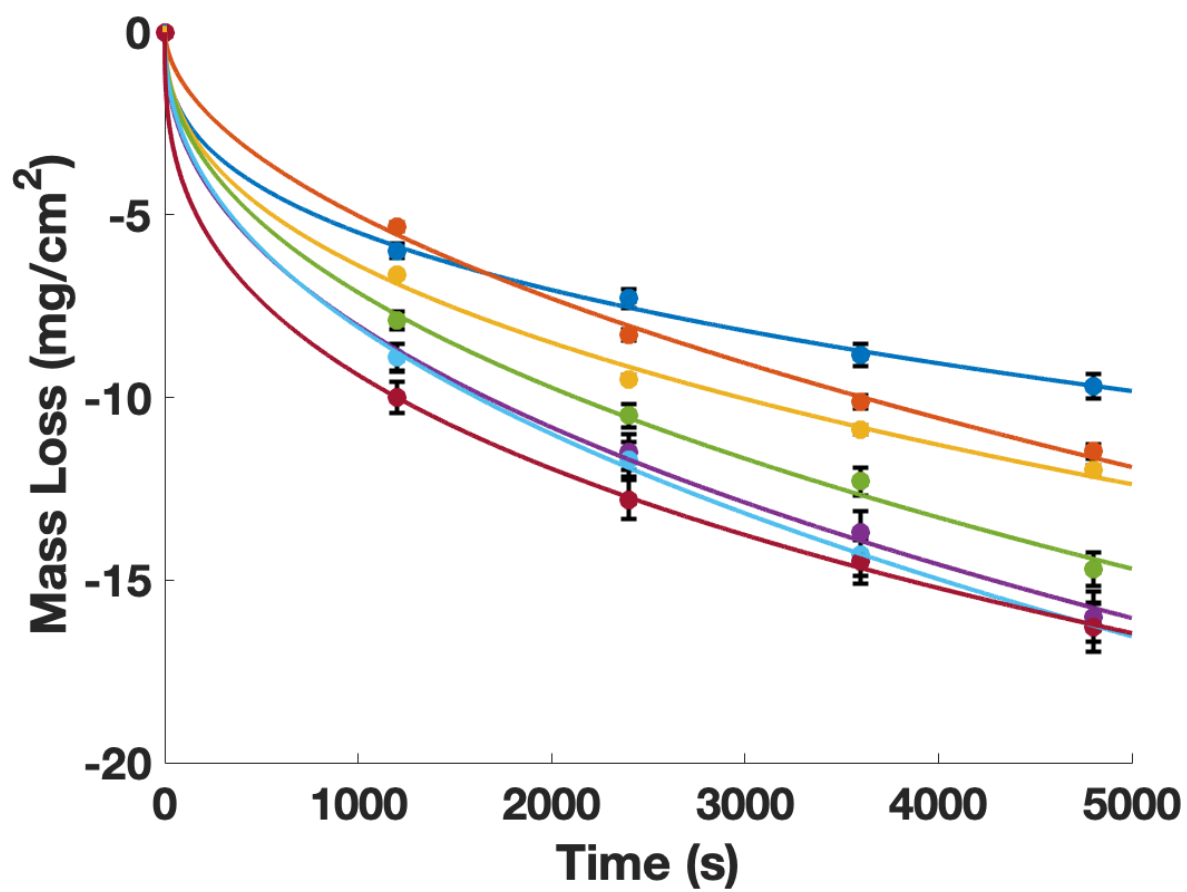
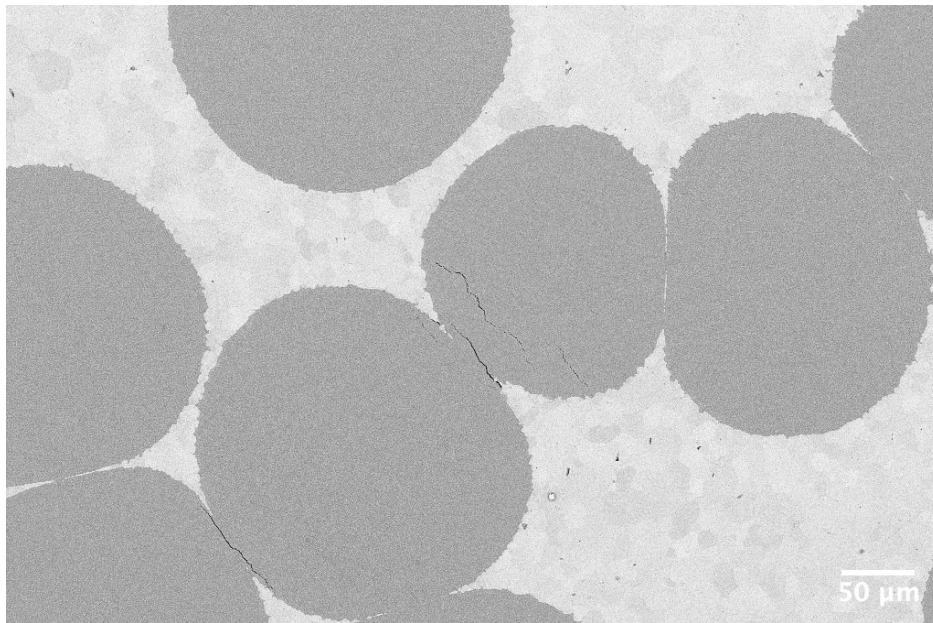
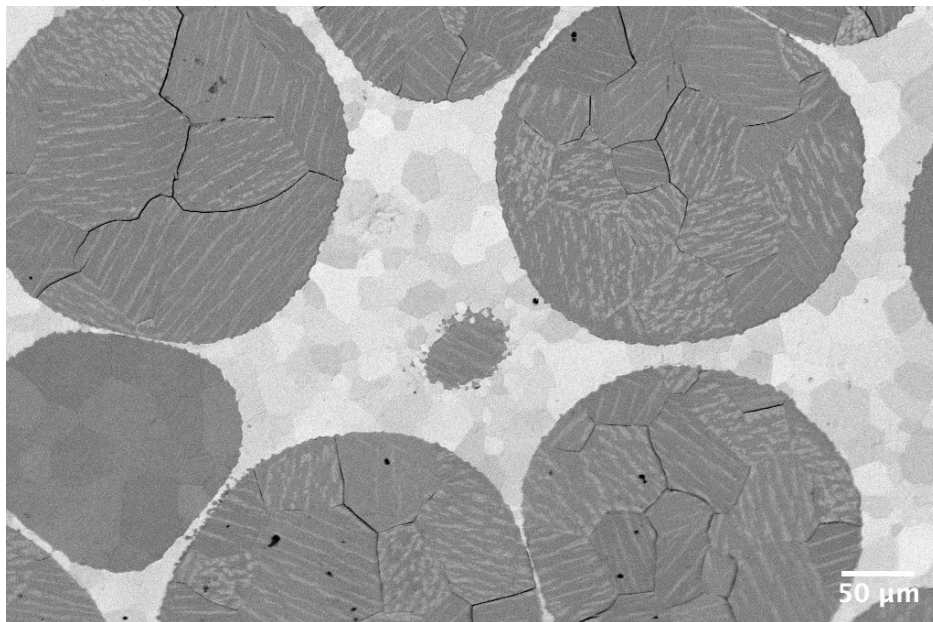


Figure 5.14: Power law fits to thermal cycled data at 2500–2630 K. Power ranges from 0.35–0.53

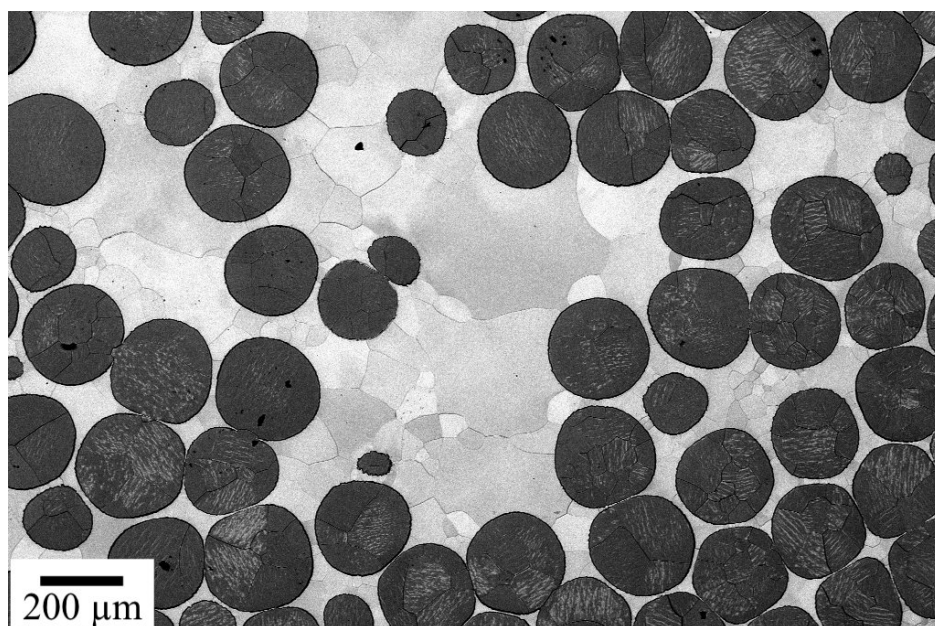


(a) BSE image of typical microstructure in a 2000 K 50% YSZ thermal cycled (TC) sample.

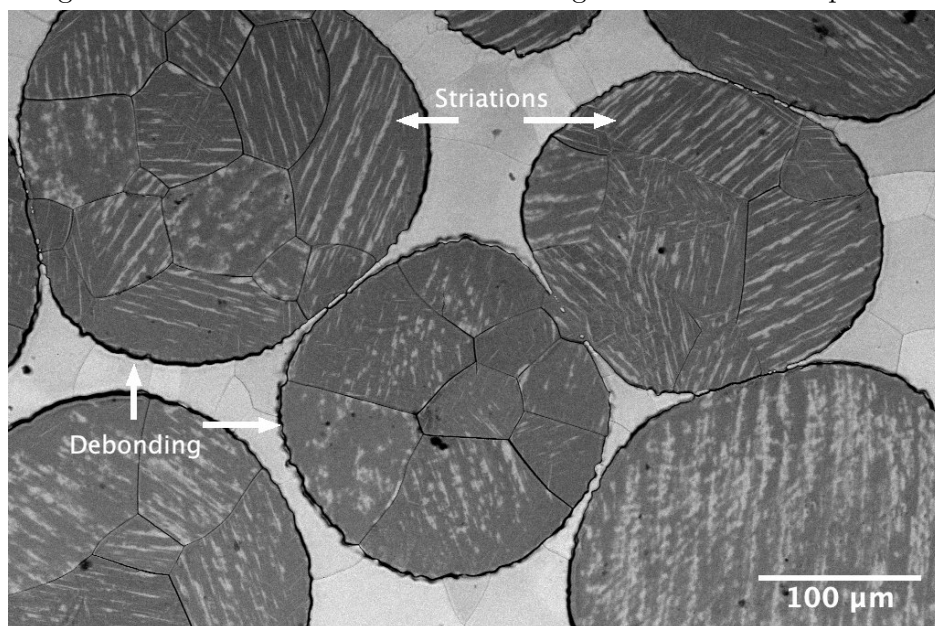


(b) BSE image of typical behavior in a 2250 K SS 70% YSZ sample.

Figure 5.15: Typical Surface Images



(a) BSE image of typical microstructure in a 2500 K SS 50% YSZ sample. Outgrowth of YSZ is observed around the edges of some ceramic particles.



(b) BSE image of Mo-YSZ cermet showing apparent debonding and laminated features in YSZ particles developed after four thermal cycles at 2500 K.

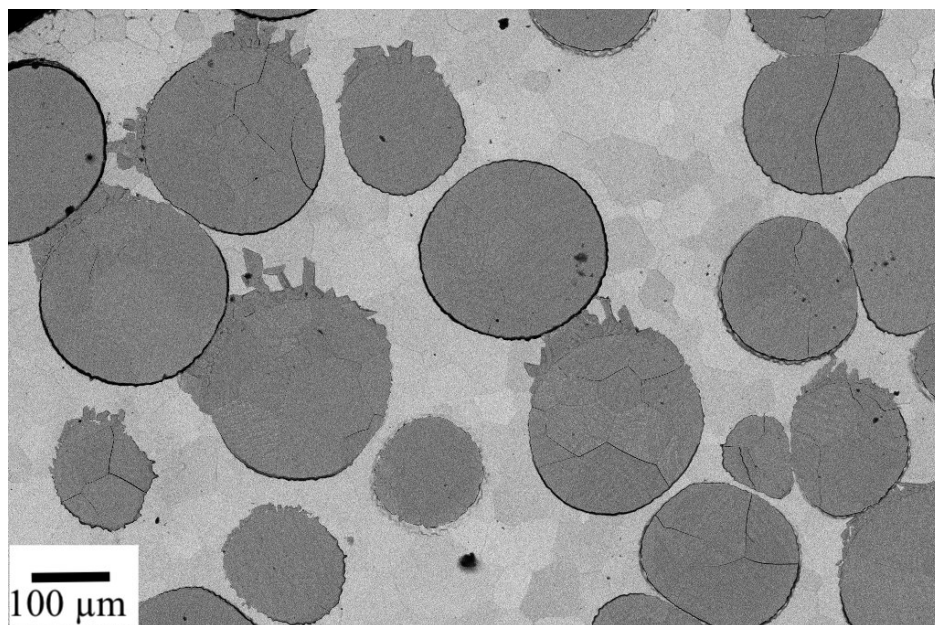
Figure 5.16: Typical Surface Images

as the formation of free Zr or Zr moving into grain boundaries, up to a maximum test temperature of 2630 K.

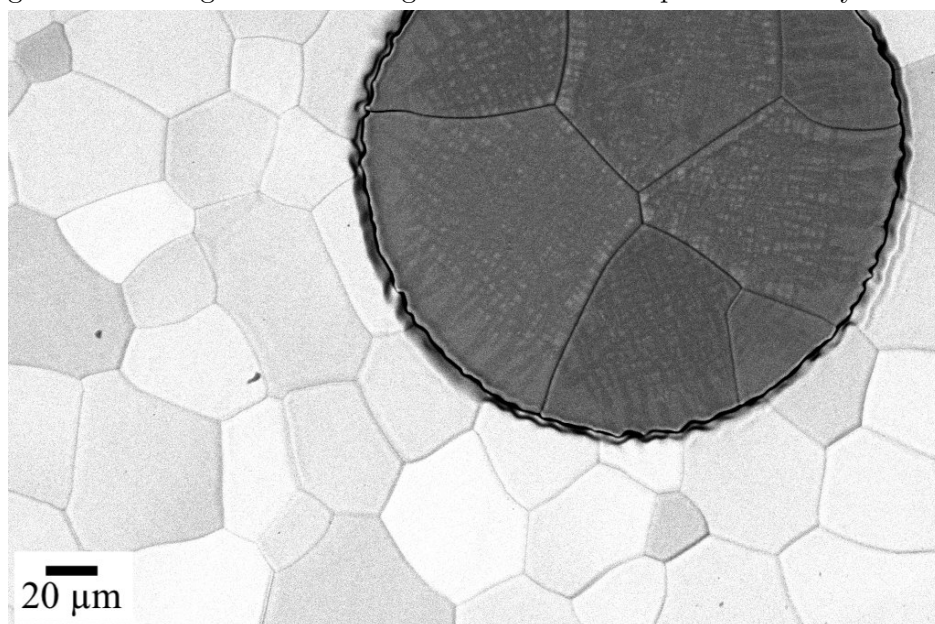
Some other regions of the 2500 K tested samples did not exhibit significant outgrowth/deposition of the YSZ particles; an example microstructure is shown in Figure 5.17a with no YSZ outgrowth but significant coarsening of the Mo grains in the central portion of the figure where there are no YSZ particles to pin the Mo grains. Figure 5.17b shows a higher magnification image of an isolated YSZ particle in a 2500 K TC sample, with apparent debonding at the surface between the YSZ and the matrix as well as displaying the typical grain sizes for both the YSZ and Mo at 2500 K. Grain boundary erosion at the surface has been observed in both the Mo and YSZ as shown in Figure 5.17b. The amount of grain boundary etching appeared to be significantly more pronounced in the YSZ particles. The amount of grain boundary erosion appeared to increase with increasing exposure temperature.

Figure 5.18 shows a 70vol% sample tested at steady-state at 2630K. A similar surface microstructure was observed for the thermal cycled sample. The 70vol% sample had significantly enhanced surface debonding/expansion of the YSZ compared to the lower (40–50%) YSZ loadings at 2630 K. The 40–50 vol% YSZ samples had a maximum YSZ-Mo surface difference $<10\text{ }\mu\text{m}$, which is similar to all sample YSZ loadings tested at 2500 K. The 70vol% YSZ sample exhibited YSZ-Mo surface height differences up to $20\text{ }\mu\text{m}$. Even particles that were cut to less than midplane could be forced above the surface by $20\text{ }\mu\text{m}$. Lower volume fractions (40–50%) had much less expansion above the surface and no instances of expansion were observed on particles that were cut to less than the midplane.

The high temperature exposure, whether steady-state or thermal cycling, produced similar temperature-dependent coarsening of the Mo matrix grain sizes compared to the initial as-sintered Mo matrix. The measured average grain size versus testing temperatures is shown for the Mo matrix in Figure 5.19a and the YSZ particles in Figure 5.19b. In general, where there are nearby bounding YSZ particles grain growth is suppressed and in open matrix locations the grain size increases more rapidly. The convergent grain size value over differing volume fraction may be biased by using areas with more Mo grains to have



(a) BSE image of typical behavior in a 2500 K TC 60%YSZ sample. Mo grain coarsening occurred in regions with low YSZ particle density.



(b) BSE image of typical surface region in Mo-YSZ 60 vol% after 4 thermal cycles at 2500 K. Moderate Mo grain size.

Figure 5.17: Typical 2500 K Images

sufficient grains to create an average grain size; these areas are less pinned and generally experience greater grain growth.

For Mo, the as sintered material had grain sizes of $6\pm 5\text{ }\mu\text{m}$. At 2000 K the grain size was $10\pm 7\text{ }\mu\text{m}$, only slightly greater than the as-sintered condition, indicating that the additional 200–300 K higher exposure temperature compared to the sintering temperature did not greatly enhance grain growth. At 2250 K the grain size increased to $18\pm 11\text{ }\mu\text{m}$ for the higher volume fractions and $34\pm 24\text{ }\mu\text{m}$ for the 40% loading. 2250 K is where the greatest difference in Mo grain size can be seen based on volume loading. At 2500 K, all volume loadings were very near the average of $46\pm 29\text{ }\mu\text{m}$.

The YSZ particles exhibited relatively rapid grain growth with increasing exposure temperature (Fig. 5.19b): $2.5\pm 1.8\text{ }\mu\text{m}$ at 2000 K (similar to the as sintered condition), $35\pm 21\text{ }\mu\text{m}$ at 2250 K and $75\pm 23\text{ }\mu\text{m}$ at 2500 K. The YSZ grain size was so high at 2630 K that many particles contain only 1 or 2 grains at the surface. The interior YSZ grain size as shown from the attacked cross-section images is dramatically smaller than that at the surface, only $49\pm 18\text{ }\mu\text{m}$ at 2630 K and appears similar at 2500 K.

The general grain growth equation with an Arrhenius relationship from eqn 5.2 is used again. Figure 5.19c and 5.19d plot the $\ln(d^n - d_0^n)$ against $\frac{1}{T} * 10^{-4}$ to derive the grain growth activation energy for Mo ($n=2$) and YSZ ($n=3$) respectively using literature values for n [117], [118]. The YSZ values use the small grain size observed at 2000K as the initial value and the activation energy is derived from the 2250–2630 K data. The activation energy for Mo in the cermet, $Q = 120\text{ kJ/mol}$, is lower but similar to that of the pure Mo sample under the same conditions in the BWXT furnace $Q = 160\text{ kJ/mol}$ and lower than the lower temperature value of $Q = 171\text{ kJ/mol}$ [117]. The activation energy for YSZ in the cermet, $Q = 190\text{ kJ/mol}$, is significantly lower than the lower temperature value of pure YSZ $Q = 520\text{ kJ/mol}$ [118].

Another interesting feature is shown in high magnification of certain areas of the Mo matrix as shown in Figure 5.20a and 5.20b. These images illustrate a mostly parallel pattern of grooves or stacking of material with spacing on the order of 200 nm. The curved shapes (particularly adjacent to grain boundaries) show that this is not an artifact from mechanical polishing. Testing on pure Mo samples showed that this preferential erosion of the Mo at high

temperature predominantly aligns with a crystallographic direction cite Mo paper. Spiral type features may be initiating at screw dislocations as has been seen in other materials [109], [110] or be associated with strain induced by the adjacent YSZ particle.

While the mass data shows slightly more mass loss with increasing surrogate fuel loadings, the microstructural characterization has not shown dramatic qualitative differences with differing YSZ particle loading. However, since the dominant microstructural changes following high temperature H_2 exposure are observed to occur within the YSZ, this is consistent with the mass loss results that the increased YSZ content leads to greater mass loss. The greatest exception is in the Mo grain growth data at 2250 K, where the 40 vol% sample had an average grain size 16 μm larger than the 50–70% samples. In addition, the overall microstructural evolution does not seem to be significantly affected by steady-state vs thermal cycling operation. Surface debonding between the particles and matrix was observed to become more pronounced with increasing temperature, with minimal effects at 2000 K and 2250 K and more pronounced separation at 2500–2630 K.

Some surface cracking was observed in the YSZ particles across the full temperature range, whereas no cracking was observed in the Mo matrix for any investigated test conditions. While some YSZ cracks were occasionally (<1% of particles) observed following fabrication and sample preparation as in Figure 5.21a, the cracking frequency was significantly more pronounced following high temperature testing. Both intergranular and transgranular cracks have been observed in the YSZ at the surface and some particles exhibited both types of cracks. An example of YSZ cracking at the surface following testing at 2250 K is shown in Figure 5.21b. The cracks are predominantly intergranular and this can be difficult to differentiate from the thermal grain boundary erosion. Some grains appear to be raised to different heights, so intergranular cracking is perhaps not the best description. Transgranular cracking is more clearly identified. Cracking in YSZ occurs in <10% of particles at 2000 K and it is difficult to differentiate TG vs IG because of small grain size and significantly less thermal etching. Many of the cracks at 2000 K happen where YSZ particles are touching. At both 2250 and 2500 K 20–30% of particles show intergranular cracks and 5–10% of particles have transgranular cracks.

To investigate the extent of the debonding between the Mo and YSZ in the near-surface region, a thin specimen wafer along the interface was created with a focused ion beam (FIB). This specimen was viewed under transmission electron microscopy (TEM) as shown in Figure 5.39a which shows a strong bond between along the Mo-YSZ interface.

Several samples were cross-sectioned to evaluate evidence of hydrogen penetration or subsurface delamination. The hydrogen penetration effects increased with increasing temperature. In the 2000 K steady-state samples, no evidence of hydrogen penetration or subsurface interface delamination was observed. Evidence for hydrogen effects included significant cracking along the grain boundaries of the YSZ particles (particularly for the 2500K samples, with over 90% of YSZ particles showing some cracking through the entire sample). The 2630 K samples had similar behavior to the 2500 K results. However, the 70% YSZ sample only had $\sim 60\%$ of the particles with visible cracking and attack. More pronounced YSZ internal cracking is evident in the bulk of the sample than at the top or bottom surfaces for 2500–2630 K. The cracking of the YSZ is extensive within the interior of the sample as shown by a cross-section for the 2500 K test temperature in Figure 5.22 and 5.35. This is contrasted to the small and faint bubble attack in the YSZ particles in the 2430 K sample (Fig. 5.23a) and pronounced YSZ particle attack in the 2630 K sample leading to significant grain fallout (Fig. 5.23b). This is similar to the behavior reported for W-YSZ cermets tested at 2750 K for 5 min [119]. The 2000 K samples did not exhibit YSZ cracking in the sample interior and the 2250 K samples had some visible grain boundaries, but cracking only appeared to occur for particles near the surface. The 2430 K samples showed both some bubbles along grain boundaries and some particles with pronounced attack, but the overall frequency was much lower than at higher temperatures ($\sim 20\%$ of particles affected).

5.2.4 Mo deposits

All tested samples show some amount of Mo that is attached to the surface of YSZ particles and is not attached to the Mo matrix. These Mo deposits are in a variety of different sizes from < 500 nm in diameter to $10\text{ }\mu\text{m}$ with a significant fraction in the $\sim 4\text{ }\mu\text{m}$ diameter range as shown in Figure 5.24. The deposit composition is confirmed to be Mo using EDS as shown in Figure 5.25b. Occasionally, these particles appear to be left over from the polishing

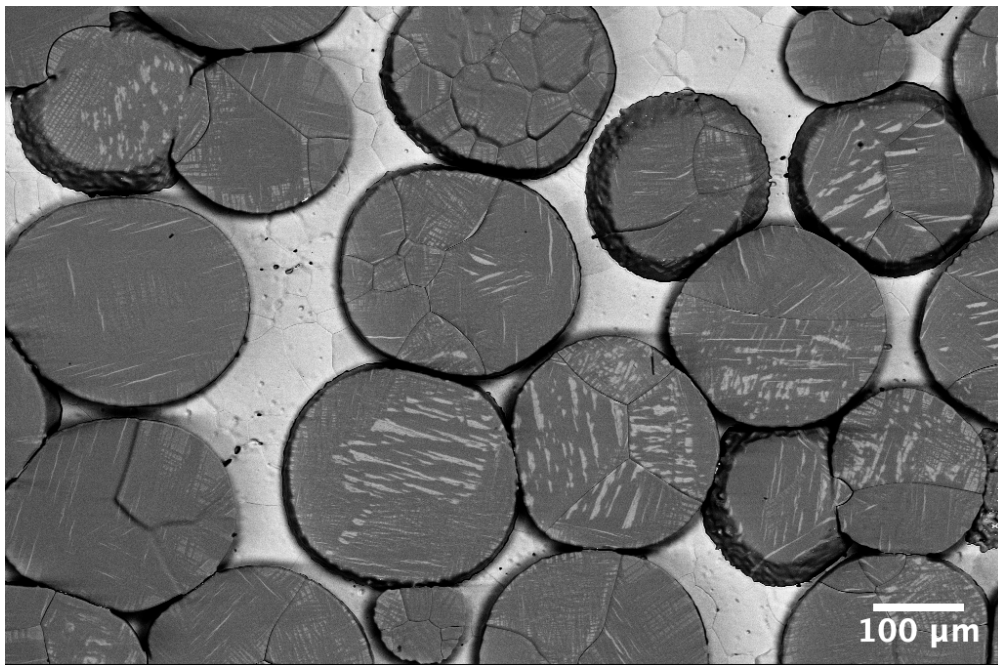
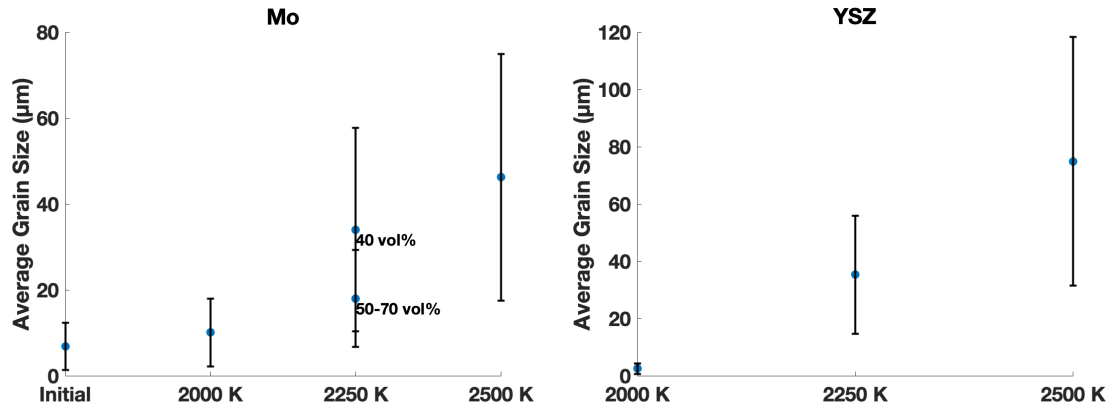
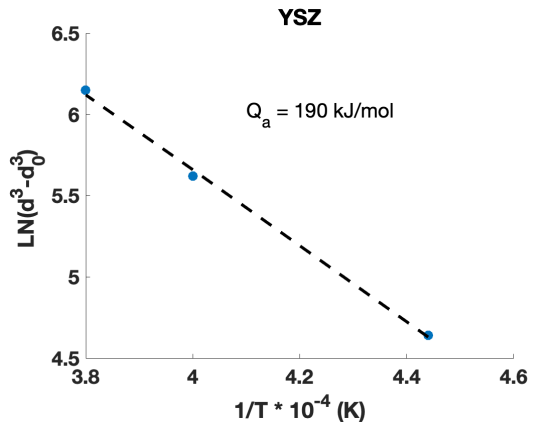
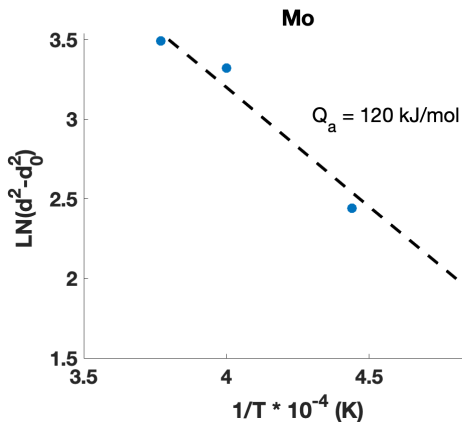


Figure 5.18: BSE of 70 vol% at 2630 K at steady-state. The 70 vol% in particular had the greatest expansion of particles above the surface $\sim 20\text{ }\mu\text{m}$ in height.



(a) Average Mo grain size

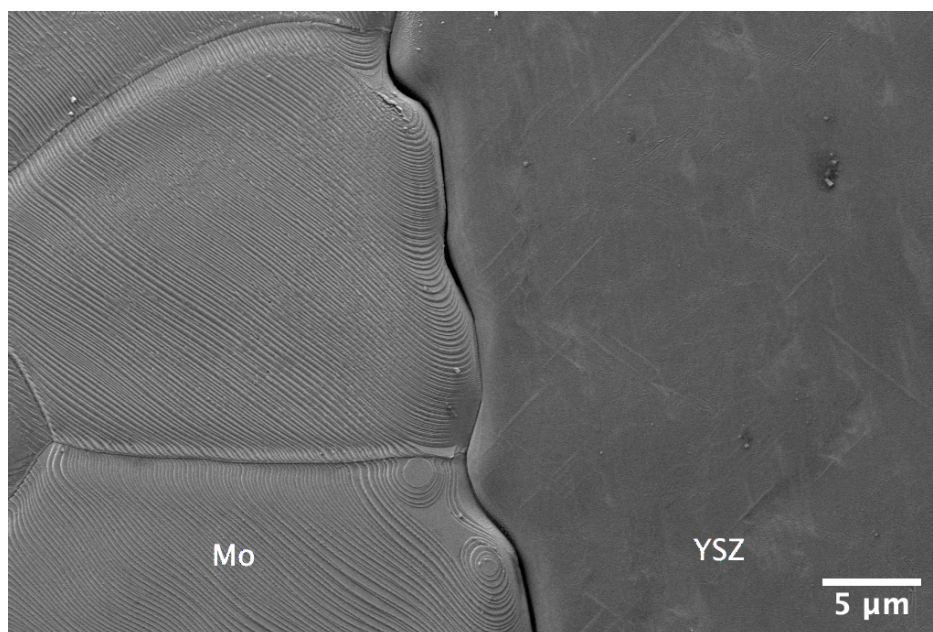
(b) Average YSZ surface grain size



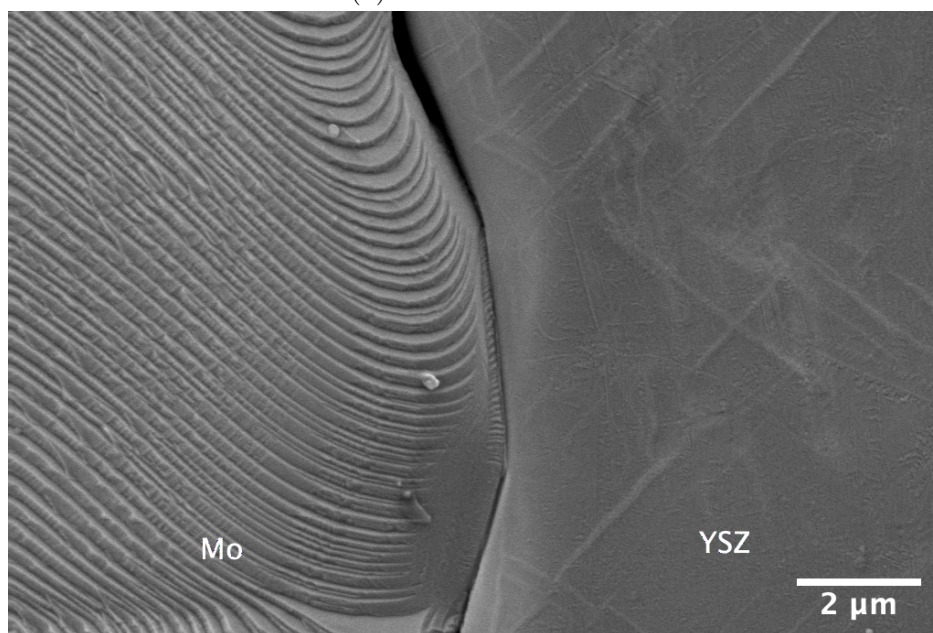
(c) Mo grain size activation energy

(d) YSZ grain size activation energy

Figure 5.19: Grain Growth in Mo-YSZ Cermets

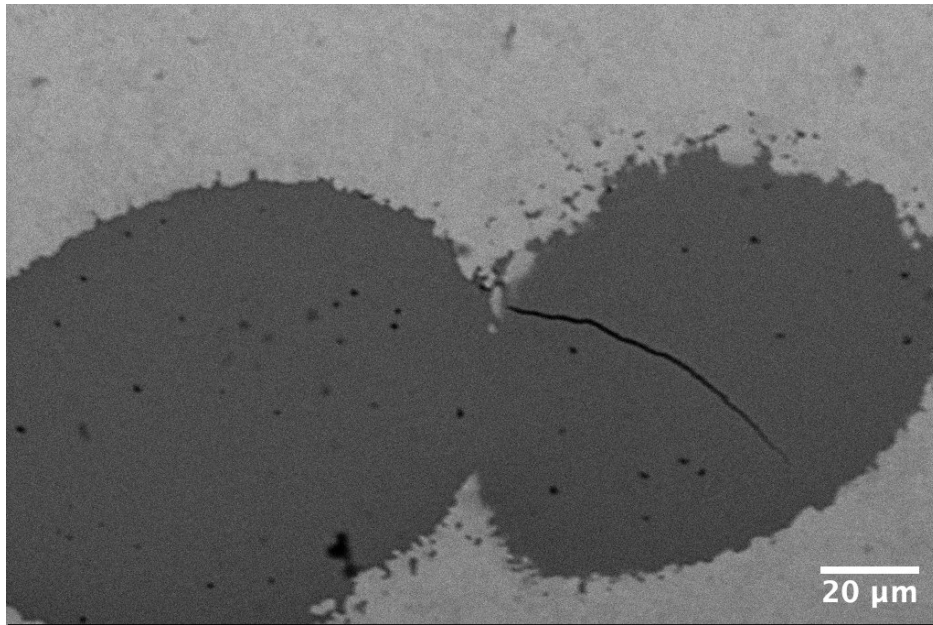


(a) 50% 2500 K TC

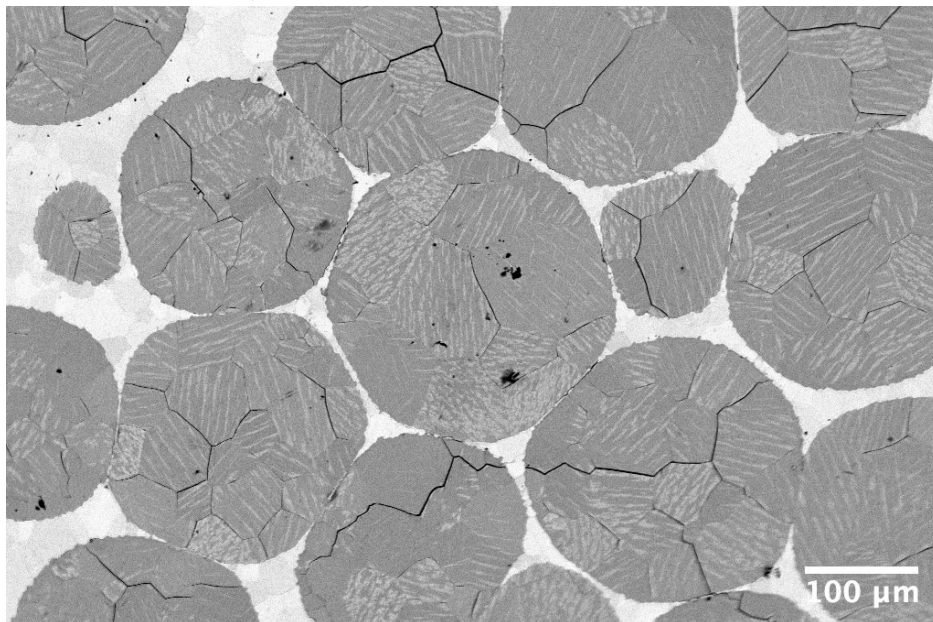


(b) 50% 2500 K TC magnified for detail.

Figure 5.20: Wavy Mo texture on the surface in 50% 2500 K TC at the interface of the Mo and YSZ. Texture is only visible at high magnification. In general, the texture seems parallel, but has curvature at the edges etc. The spacing between layers is on the order of 200 nm.



(a) Examples of surface cracking in YSZ before testing 50%YSZ (observed in <1% of particles)



(b) Examples of surface cracking in YSZ after testing at 2250K for TC 70%YSZ (cracks observed in >50% of particles)

Figure 5.21: YSZ Surface Cracking

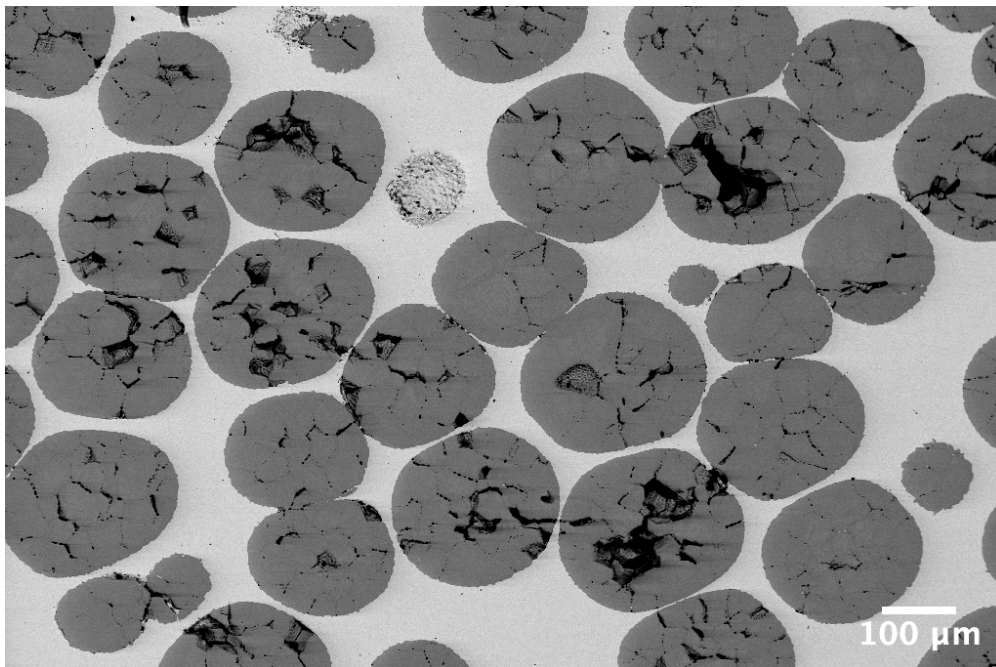
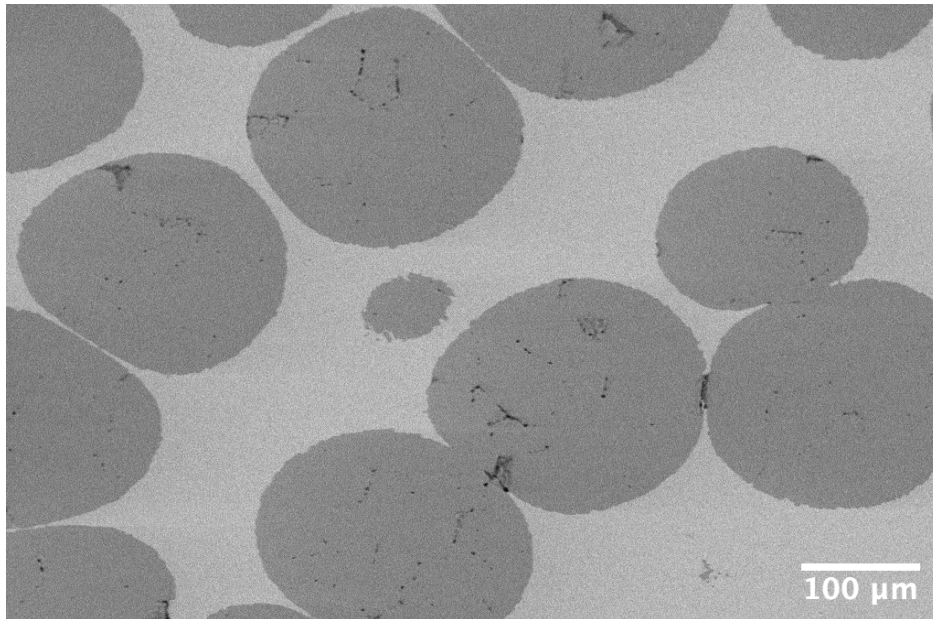
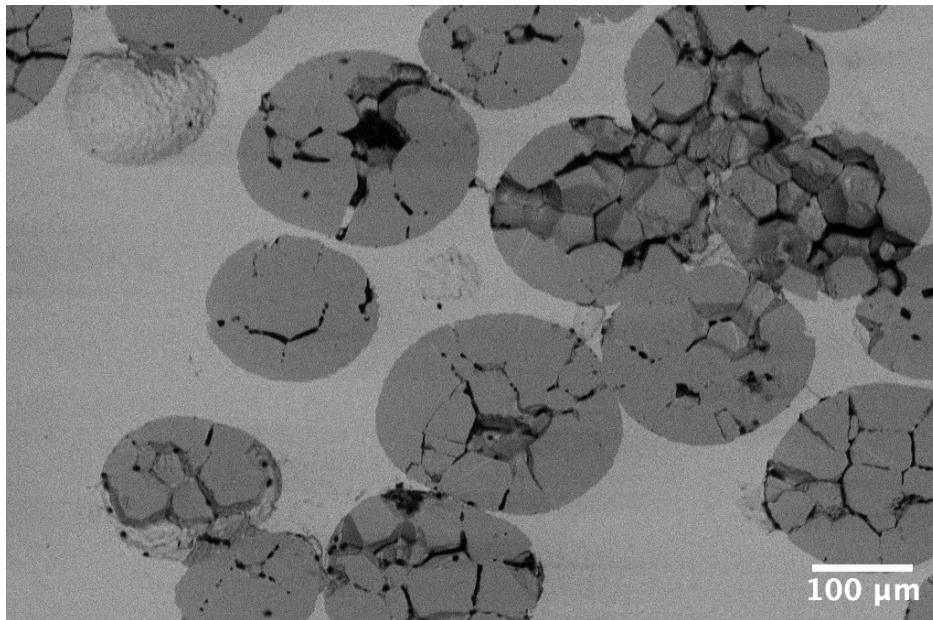


Figure 5.22: Example of interior cracking along grain boundaries throughout the interior of the sample leading to some grain fall-out after cross-sectioning and polishing. Cross-section of 2500K TC 60%YSZ.



(a) Cross-section of 2430K 60% Steady-state. Small bubble-like attack along grain boundaries. This is much fainter and less frequent than for higher temperatures.



(b) Cross-section of 2630K 50% Steady-state. Significant attack along grain boundaries leading to pullout of grains within the YSZ spheres with polishing.

Figure 5.23: Bubble Attack

process as the Mo is worn down to uncover a YSZ particle below the surface; however, the majority appear to be deposited on the surface from elsewhere. Many of these Mo deposits are spherical, however some have clearly visible crystalline faces as shown in Figure 5.26.

Previous analysis of Mo cermets for NTP have concluded that the vapor pressure of Mo becomes significant above 2470 K [50]. The loss of Mo matrix material is a very important effect as the matrix gives structural stability to the cermet. Erosion of the metal matrix will determine the mechanical properties and durability of the fuel system. When these effects were first observed at 2000 K with a quick 5 min scoping test, it was thought that the Mo on the surface could be melted Mo oxides that were formed during the sample preparation process. With subsequent samples, additional care was taken to ensure no visible oxide layer was present on the surface of prior to testing; however, the deposits persisted. These Mo deposits are distributed randomly along the surface, but are most easily located on the YSZ particles. In samples that have significant ZrO_2 redeposition regions, there is often a significant concentration of Mo deposits on top of the YSZ deposit as shown in Figure 5.24. Raman analysis of these deposits showed no signal over background demonstrating that they are not Mo oxides, but metallic Mo.

5.2.5 Zirconia Deposits

Zirconia deposits were found in several regions and have been observed with preferentially higher frequency near the outer circumferential edge of the samples and not near the center of the test stand. This suggests they may be deposited based on the flow pattern of the H_2 in the chamber of CFEET, or spalling off after being deposited on the chamber wall. Benensky et. al. showed that deposits of some type can adhere to the inner wall of the susceptor in CFEET following high temperature hydrogen testing of some materials [120]. These ZrO_2 deposits are observed almost exclusively on the Mo surface. They have crystalline faces unlike the predominantly spherical Mo deposits. An example of these deposits is shown in Figure 5.28a and figure 5.27. These deposits seem to differ from the growth of neighboring YSZ over the surface in Figure 5.28b. The growth of new crystals from the central YSZ sphere is a commonly noted behavior in these samples and it is theorized that it occurs at high temperature when the YSZ sphere expands above the surface of the Mo due to

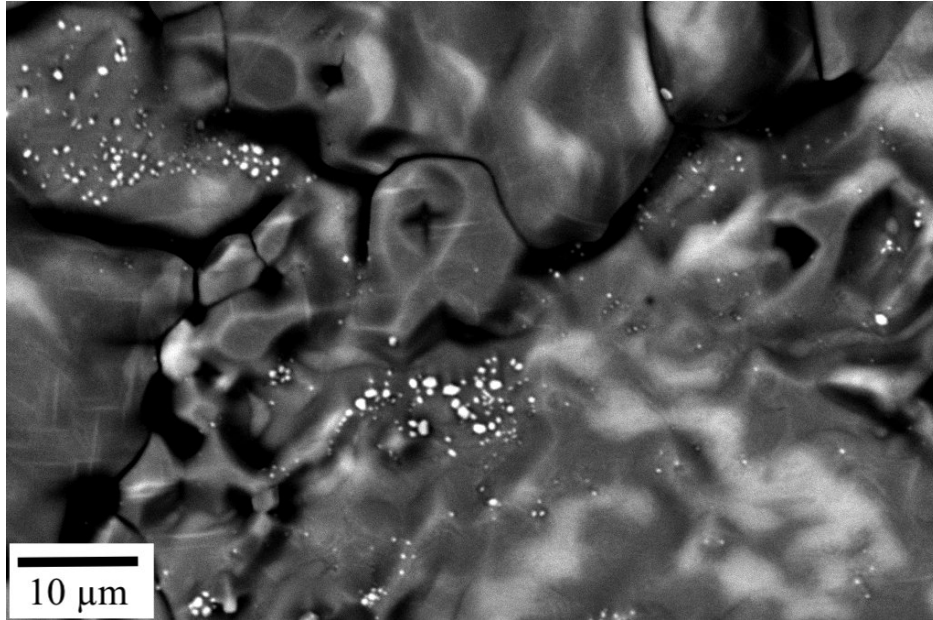
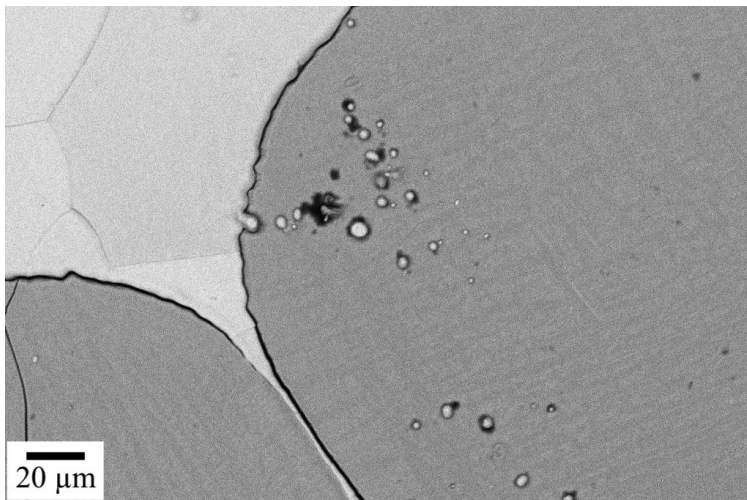
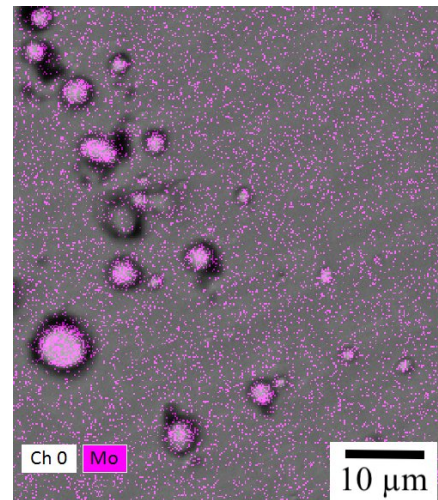


Figure 5.24: Mo deposits (small bright spots) on top of the thick Zr high deposition region - 2500 K TC 40%



(a) BSE image



(b) EDS map

Figure 5.25: BSE image of Mo deposits (small bright spots) - 2500 K SS 50% with EDS map highlighting the Mo

relatively higher thermal expansion. EDS has confirmed the composition as Zr rich. Raman analysis indicated that the extensions in Figure 3b are tetragonal ZrO_2 like the starting YSZ material. The dispersed deposits are shown by Raman to also be predominantly tetragonal ZrO_2 , but have indications that the amount of yttria present may have decreased. Other surface regions show peaks for monoclinic ZrO_2 .

Additionally some of these Zr deposits are sitting in eroded Mo grain boundaries near the edges of the samples in 2250 K TC 40% in Figure 5.27. Cross-section examination of samples following H exposure have not shown this behavior to penetrate below the surface.

In other parts of some samples, significant deposition of ZrO_2 was observed in roughly circular areas. These were first observed in both steady-state and thermally cycled samples at 2000 K. Typically 1 to 2 of these regions appeared to evolve in each thermal cycle at 2000 K, so following a full thermal cycle series 7-8 of these regions are distributed among the 4 sample surfaces. In contrast, only one region each was found in all of the 2250 K and 2500 K tests in CFEET and none were observed in the BWXT furnace. These circular deposits range in size from ~ 1.5 mm diameter at the largest in the 2000 K samples to $\sim 100\mu\text{m}$ in later samples. From observation through the monitoring camera viewing the sample surface during CFEET operation, these deposition regions seem to evolve in the first few minutes during testing, perhaps even before steady-state temperature is reached.

In these intense deposition regions there is a large amount of material scattered on the surface as shown in Figures 5.29–5.31. These deposits are shown by both optical microscopy and secondary electron imaging to be raised above the polished sample surface. Figure 5.30b is an enlarged area from figure 5.30a with an overlaid EDS map illustrating that the distributed material is rich in Zr.

Within the intense deposition areas tested at 2000 K, the apparent grain size of ZrO_2 particles is significantly smaller ($\sim 5\ \mu\text{m}$) than in the bulk (15–50 μm) as shown in Figure 5.29b. The YSZ grain size difference could be a temperature-based effect comparing the 2000 K tests with 2250 and 2500 K and not due to the excess Zr deposition. These high damage areas in the 2000 K tests both have material eroded away from the surface of the ceramic particle and material redeposited above the surface of the Mo matrix. These YSZ grains also are significantly less connected to their neighbors and create a very textured surface below the

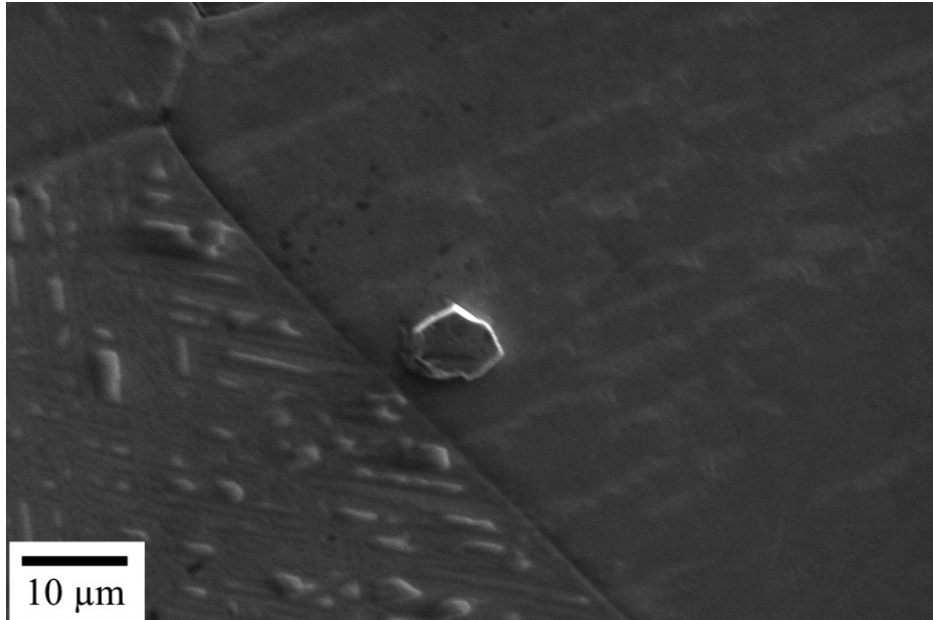


Figure 5.26: SE image of crystalline Mo deposit - 2500 K 70% SS

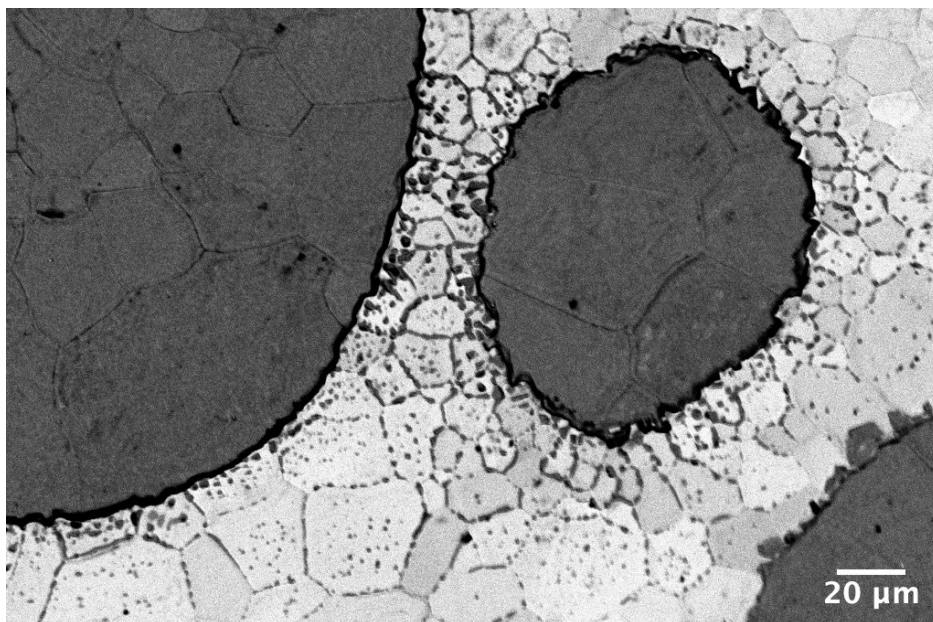
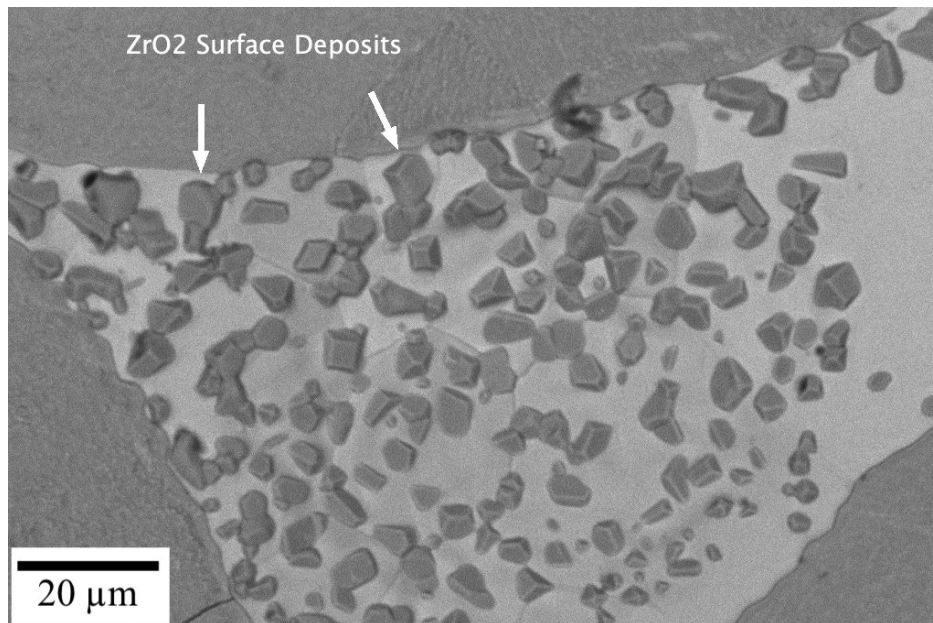
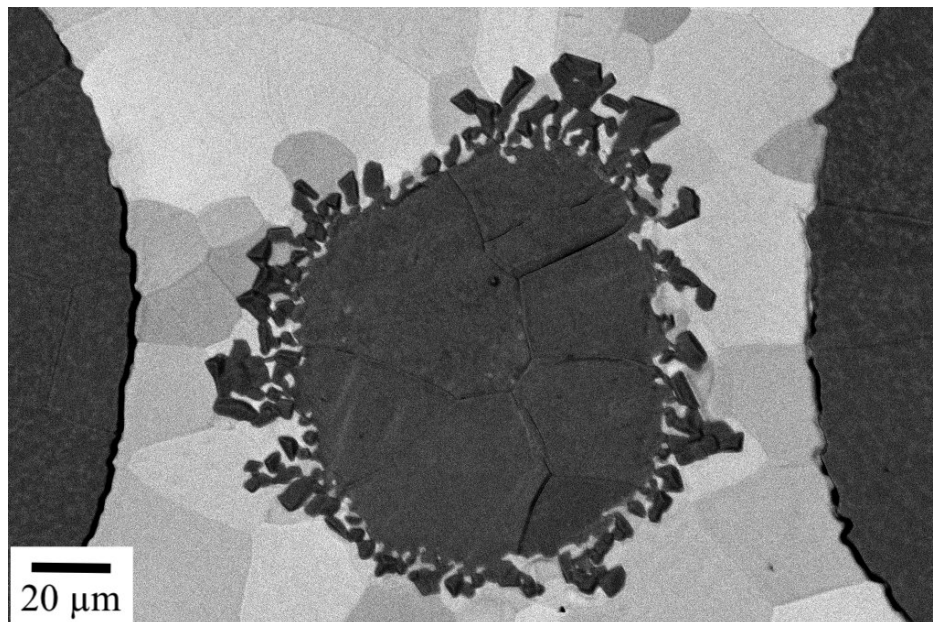


Figure 5.27: Zr deposits in eroded Mo grain boundaries near the edges of the samples in 2250 K TC 40%YSZ. This is the only sample with regions that look like this.



(a) ZrO₂ deposits concentrating on Mo surface near the sample edge - 2500 K SS 70%YSZ



(b) New ZrO₂ crystals growing from a fuel sphere onto the Mo surface - 2250 K TC 40%YSZ

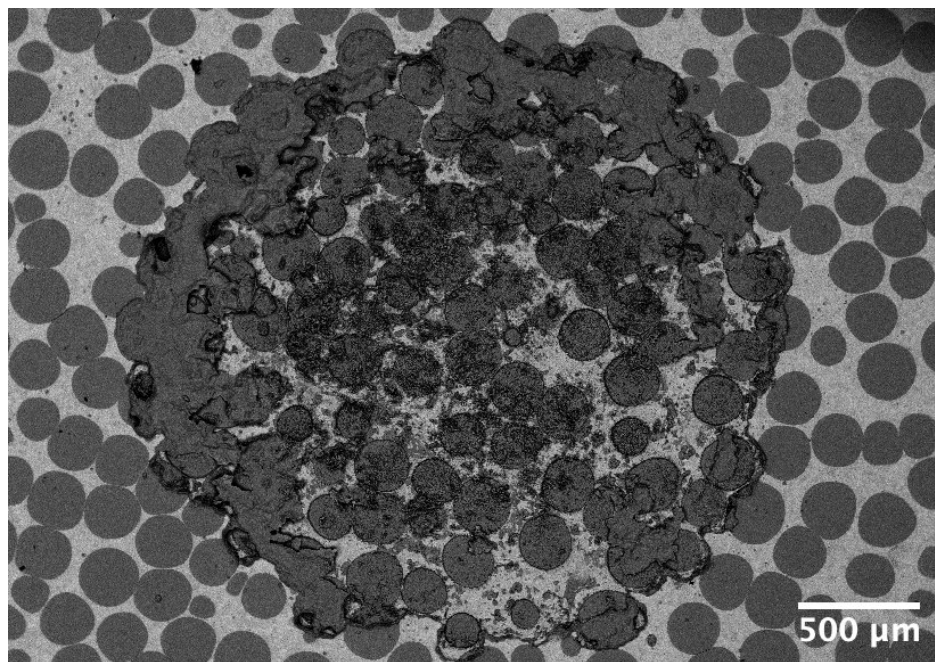
Figure 5.28: ZrO₂ Deposits

level of the metal matrix. This is different in appearance to intergranular cracking between YSZ grains which has been observed in other regions. The 2000 K tested samples had a worse surface finish compared to subsequent samples and the additional surface undulations and scratches in the YSZ prior to testing may have enhanced corrosion due to the increased surface area exposed to H_2 . It is possible these regions have been formed by debris particles from a previous test or eroding BN from the insulator in CFEEET that is disturbed in the vacuum chamber when the H_2 gas is first introduced and falls on the sample surface[120]. This debris could then act as a nucleation site for eroded YSZ material to concentrate onto even if the original debris is destroyed or removed.

When these circular depositions have occurred in the 2250 and 2500 K tests they do not show this grain size difference or the significant erosion of the ceramic particle below the level of the Mo matrix. The 2000 K localized deposition areas have a thick deposited layer of this ZrO_2 material as shown in Figure 5.29a while in the majority of subsequent samples the circular region is much more like an area of small $\sim 2\mu m$ crystal deposits as shown in Figure 5.31a. The thick deposition regions are very dark when reflecting optical light as shown in Figure 5.31b, however at a glance they appear white and cloudy much like the original ZrO_2 spheres prior to sintering. All of these various types of ZrO_2 deposits and some observed Mo deposits are purely a surface feature. No evidence for these specific features exists below the surface in a cross-sectioned sample.

Some YSZ grains have a raised texture which is sporadic within the grain. An example is shown in Figure 5.32. These are primarily at the higher temperature tests (2500 K+). They do not seem to correlate with the striation behavior discussed later. Since they are apparent in the secondary electron image they could also be related to charging of the surface in specific areas.

There is significant expansion of the YSZ above the surface level at high temperature and high volume loadings. This debonding behavior is shown in Figure 5.33a for a steady-state 2500 K exposure of a 60% YSZ sample. Height differences of 20+ μm have been observed in the 70 vol% sample tested at 2630 K as shown in Figure 5.34. Crystal growth at the surface between neighboring YSZ spheres has also been observed at the 2630 K temperatures. This

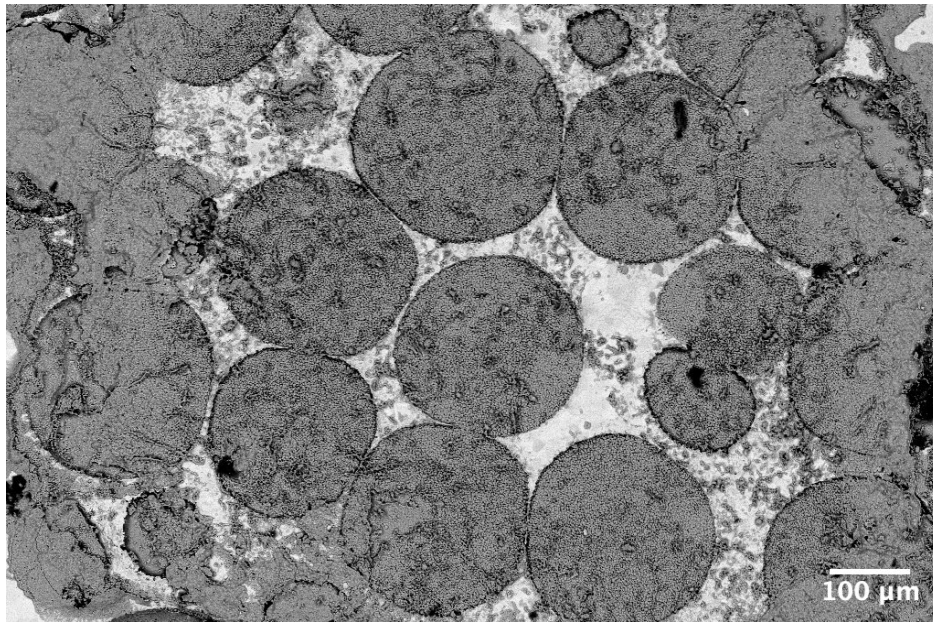


(a) BSE image of significant ZrO₂ deposition region in 60 vol% after 4 thermal cycles at 2000 K.

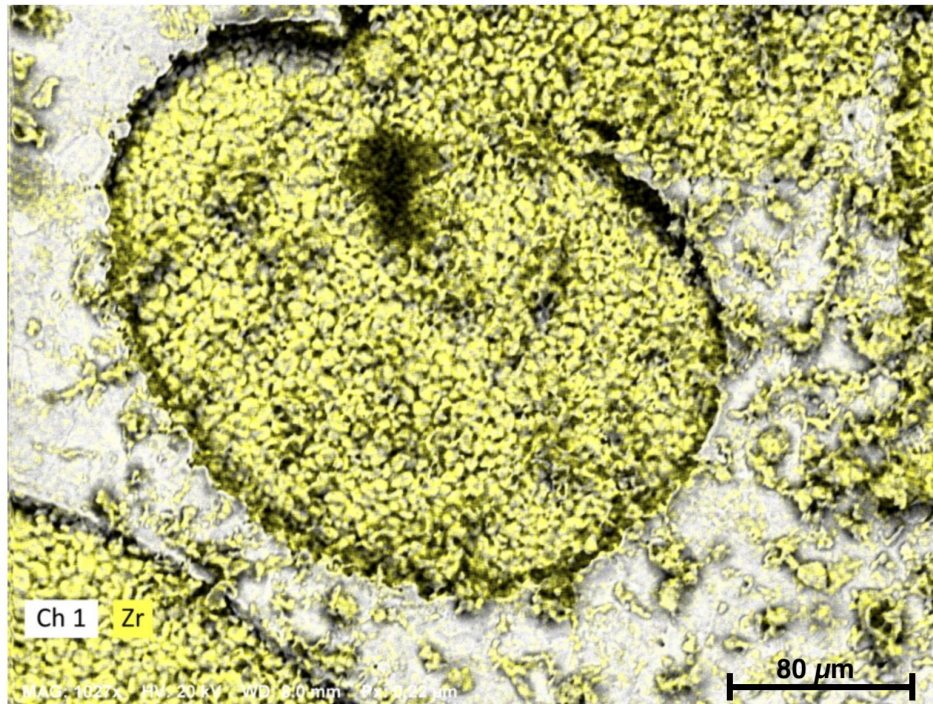


(b) BSE image of significant deposition region in 60 vol%YSZ after 4 thermal cycles at 2000 K. Shows preferential hydrogen attack around the YSZ grain boundaries which are quite small (5–10 μm).

Figure 5.29: Large ZrO₂ Deposits



(a) BSE image of significant ZrO_2 deposition region in 70 vol% after 4 thermal cycles at 2000 K.

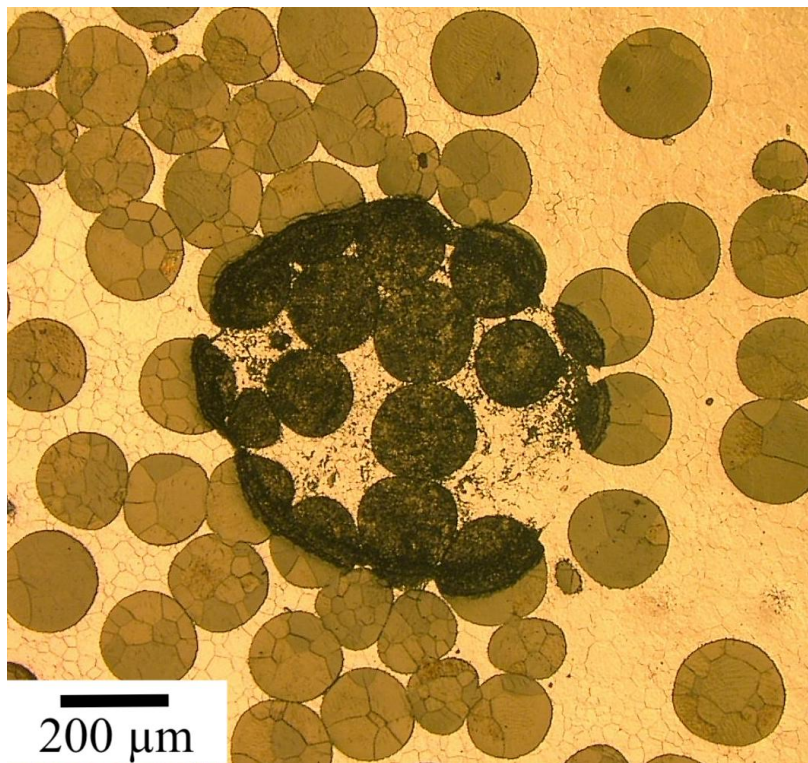


(b) EDS highlighting the Zr rich deposits

Figure 5.30: ZrO_2 Deposits



(a) Secondary electron (SE) image of small ZrO_2 deposition region of the 60%YSZ sample under thermal cycling at 2250 K.



(b) Optical image of high damage region of the 40%YSZ sample under thermal cycling at 2500 K. Shows the ZrO_2 deposit is optically dark.

Figure 5.31: ZrO_2 Deposits

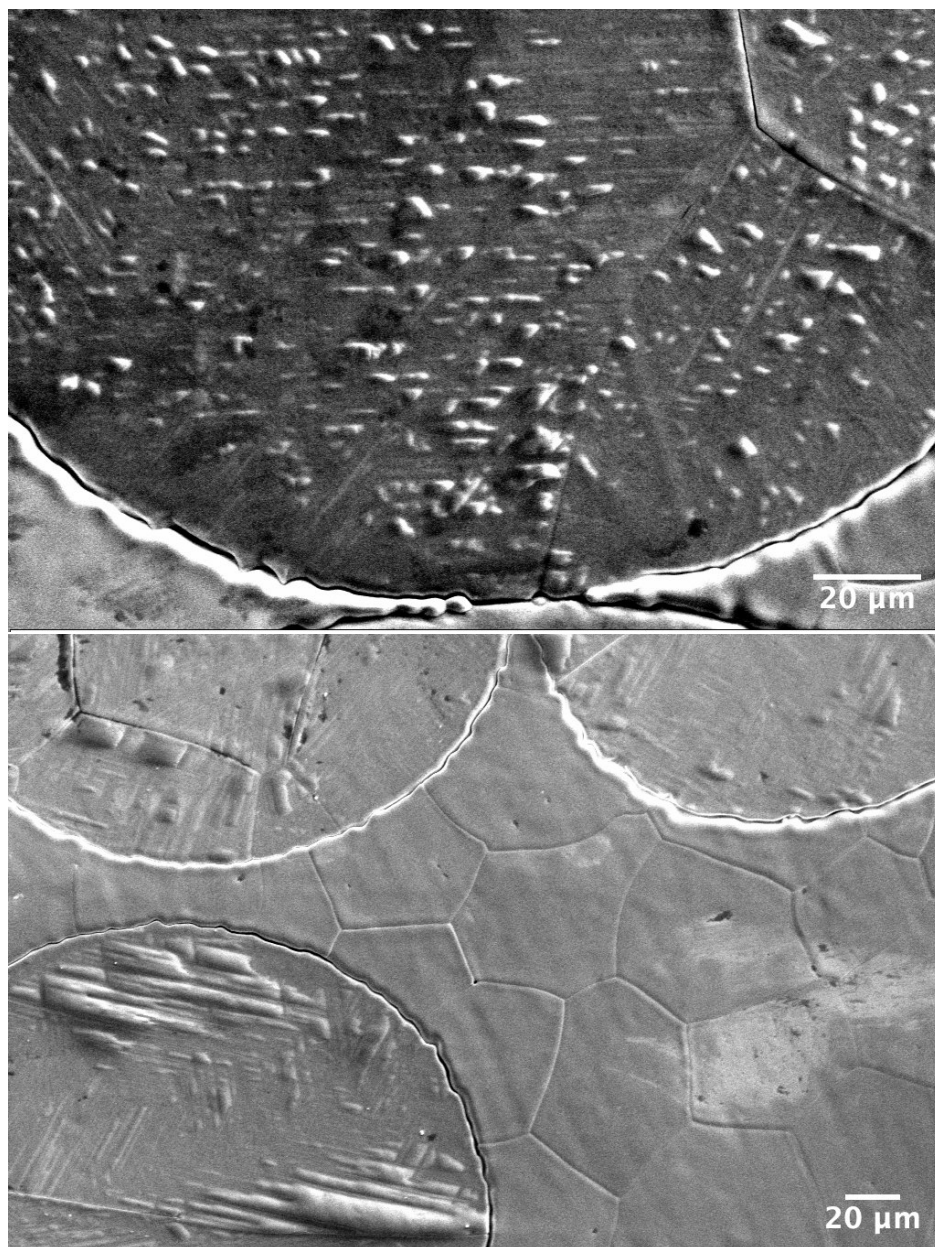


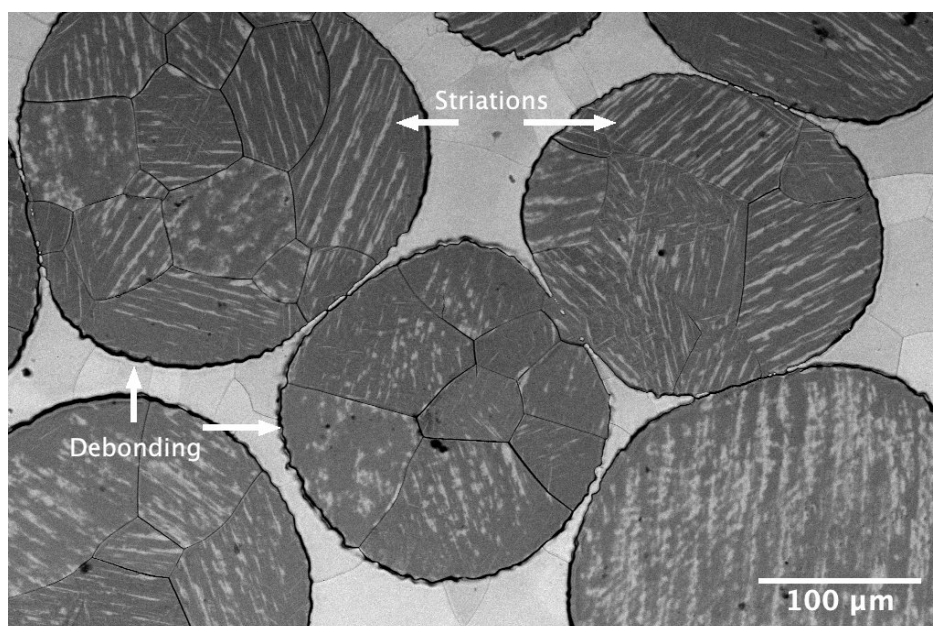
Figure 5.32: Raised features or charging within the YSZ grain apparent in the secondary electron image. These do not seem to be ZrO_2 deposits from elsewhere - 2500 K SS 60%YSZ. Some sort of uneven expansion

is likely occurring when the YSZ particles are raised above the surface level and can then contact a neighboring sphere and the new crystal growth can occur.

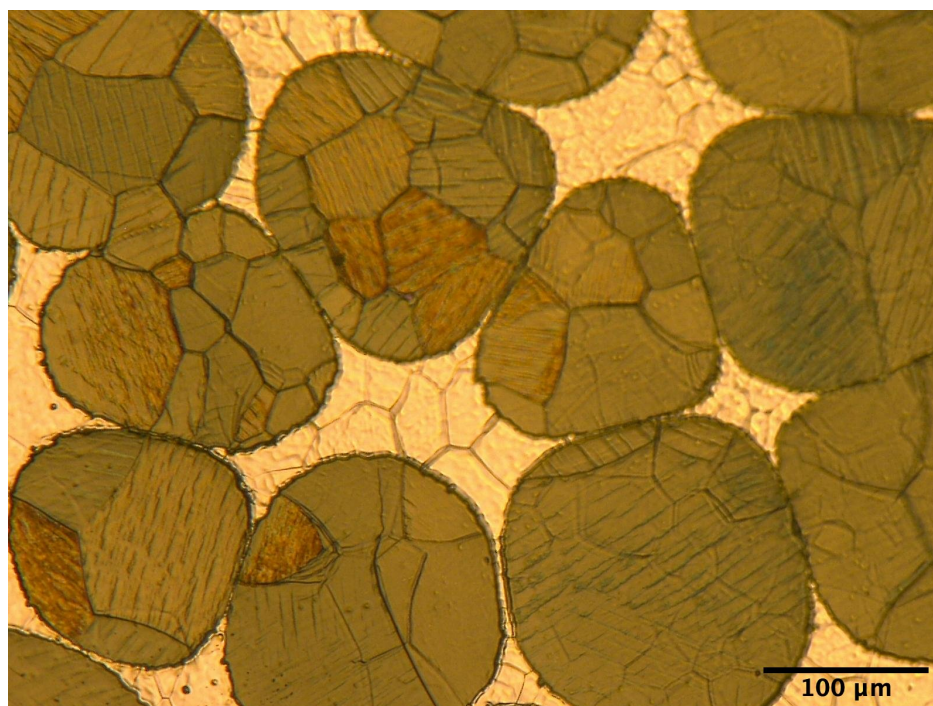
5.2.6 Features Throughout Sample and Subsurface

Significant cracking features were visible in cross-sectioned samples as shown in Figure 5.35–5.36. This attack on the YSZ was apparent in cross-sections for samples tested at 2430–2630 K with more frequent attack at 2500 K and 2630 K than for 2430 K. At 2250 K there was not visible erosion in BSE images; however, the grain boundaries in the YSZ were distinctive in SE images which is not visible in pretest samples likely indicating that there is some amount of H_2 interaction with the grain boundaries even at lower temperatures. If the system only contained YSZ, as in Figure 3.1, the bubbles may be explained by the water vapor but would not have a preferential drive to the YSZ grain boundaries. Another factor is the potential interaction with aluminum oxide which is present in small amounts in the YSZ (0.25 wt%). The Al_2O_3 is likely used as a sintering aid and would preferentially be found along the YSZ grain boundaries. Al_2O_3 has a melting point of 2345 K and for the high temperature tests will be liquid and also migrate to the grain boundaries. Based on the Gibb’s free energy calculations from Figure 3.2 the inclusion of even a small amount of alumina significantly increases the concentrations of gaseous products including water vapor and so the aluminum oxide may be where the reduction and gas formation is preferentially taking place.

The erosion along these grain boundaries throughout the sample suggest H_2 is fully penetrating the sample at 2500–2630 K. A simple estimate of hydrogen diffusion for these samples and temperatures using $x = \sqrt{DT}$ with a hydrogen diffusion coefficient in Mo extrapolated from lower temperature data[62], $D = 4.0 * 10^{-8} \exp \frac{-22.3kJ/mol}{RT} \left(\frac{m^2}{s} \right)$, shows that H_2 should diffuse through 3–4 mm of Mo for 20 min exposures at 2000–2500 K. Other diffusion coefficient values predict a H diffusion distance of 12 mm[121]. These values indicate that the entirety of the subscale samples used in this study should be exposed to the H_2 during the experiment across the entire temperature range. These same hydrogen diffusion calculations for the YSZ particles have more mixed results, due to uncertainties in the hydrogen diffusion coefficients for tetragonal YSZ. Using the diffusion coefficient reported for a cubic-YSZ[122] a 20 min exposure at 2500 K could penetrate greater than 250 μm and



(a) BSE image of Mo-60%YSZ cermet showing apparent debonding and laminated features in YSZ particles developed after four thermal cycles at 2500 K.



(b) Optical image of Mo-50%YSZ cermet showing striations on the surface of the YSZ after a single thermal cycle of 20 min at 2500 K.

Figure 5.33: Debonding and Striations

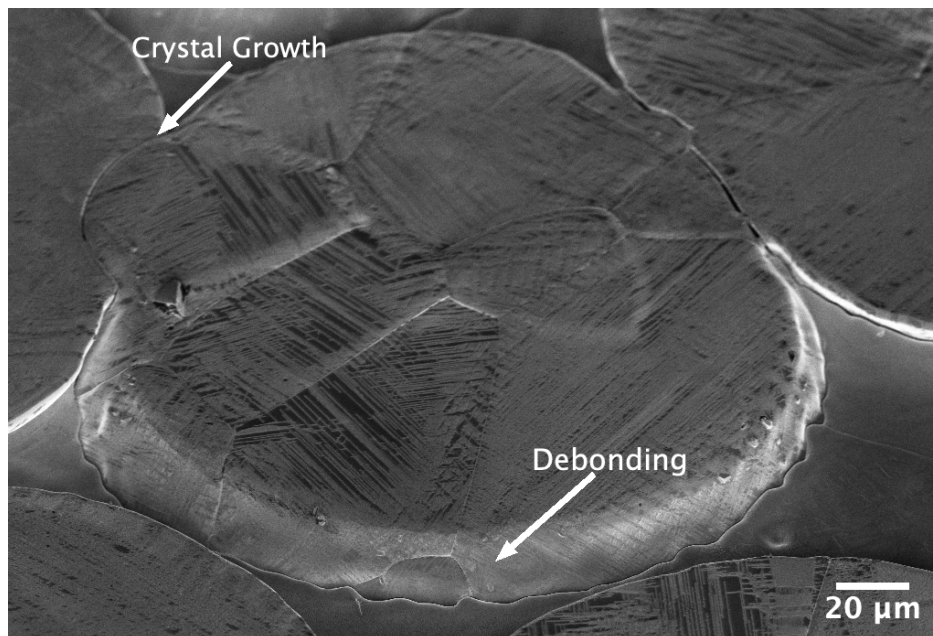


Figure 5.34: SE image taken at a 45-degree tilt to highlight YSZ debonding at surface including the raised height in the YSZ above the Mo surface, showing up to 20 μm in height. This image also shows crystal growth occurring above the surface between neighboring YSZ spheres. 70 vol% 2630 K TC.

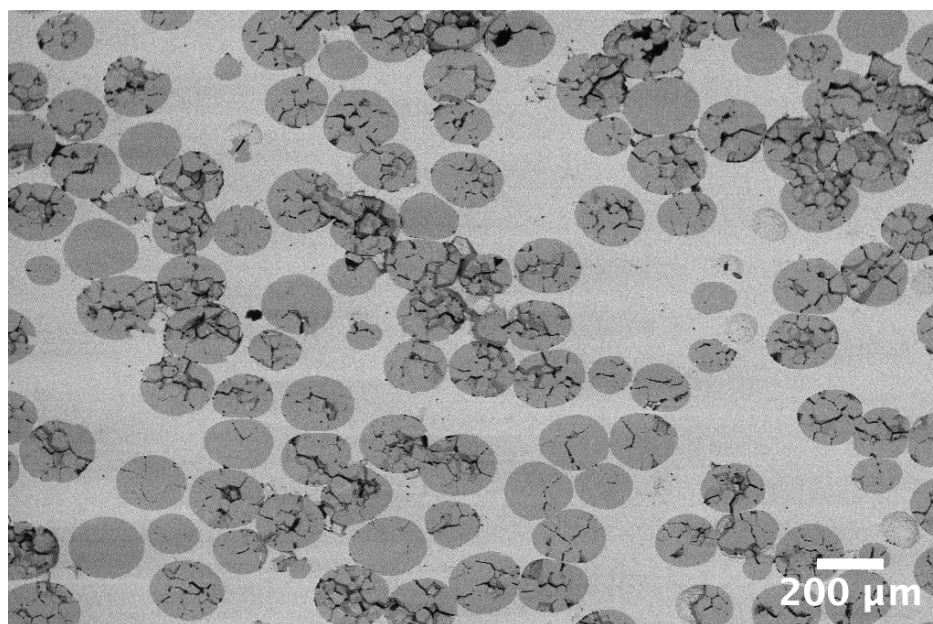
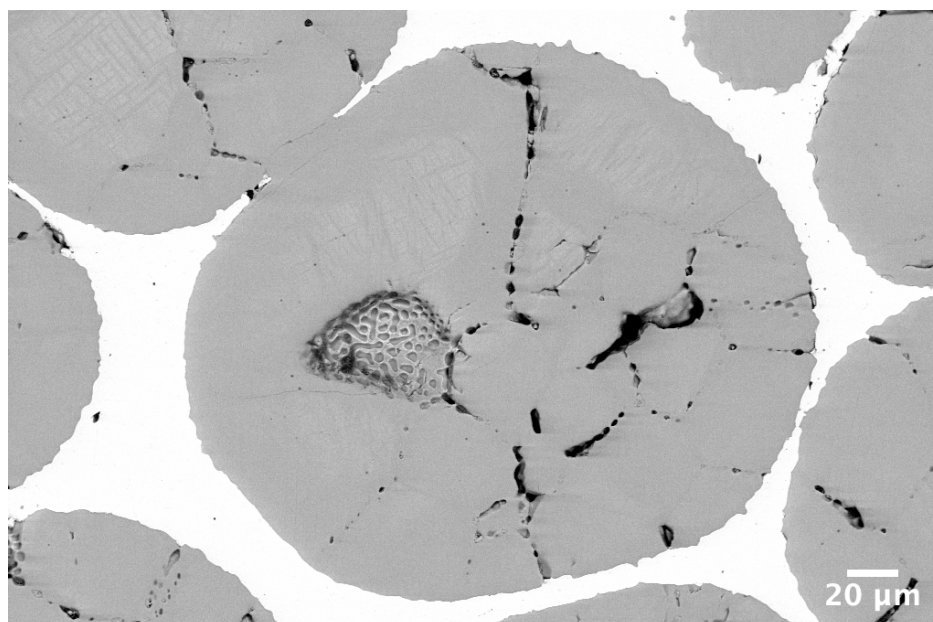
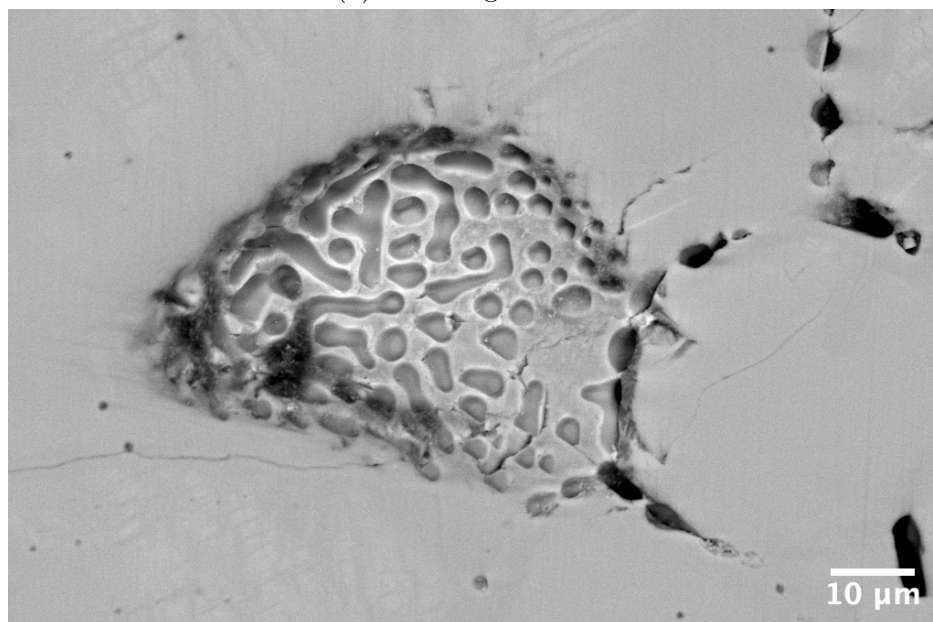


Figure 5.35: Cross-sectioned sample showing hydrogen interaction throughout the interior of the sample. 90% of YSZ particles show H_2 attack along grain boundaries and the erosion is extensive for the majority of particles. From a cross-sectioned sample tested at 2630 K SS 50vol%.



(a) Low magnification



(b) Higher magnification

Figure 5.36: Cross-sectioned sample showing hydrogen interaction with the YSZ below the surface. Bubble-like attack on the grain boundaries of the YSZ. Particularly noticeable after grain fallout. From cross-sectioned sample tested at 2500 K TC 70vol%.

therefore it is expected that the full YSZ particle would be exposed. However, for ZrO_2 oxides grown on various zirconium alloys the reported range of the H diffusion coefficients span several orders of magnitude[123], [124]. This same 20 min exposure at 2500 K can produce values from $5\mu\text{m}$ up to 1mm depending on the starting Zr-based alloy.

XRD was used to investigate if significant new phases were introduced after the high temperature exposure to H_2 . The blue XRD spectra shown in the lower portion of Figure 5.37 is representative of all samples before and after testing with the exception of centering the X-ray beam on a large Zr deposition region. The specific spectrum in Fig. 5.37 was collected on the 60 vol% sample thermal cycled at 2000 K. The blue spectra was obtained from the x-ray beam centered on a surface section with no deposits while the red spectra (upper portion of Fig. 13) was obtained from centering on the large deposition area. Analysis of the bulk (blue) spectra indicates that the ZrO_2 is in a tetragonal state typical of YSZ with 5.7 mol% $\text{YO}_{1.5}$ both before and after testing. The spectrum centered on the high deposition region (red) shows a new peak at 28.2° . This peak indicates the presence of monoclinic phase ZrO_2 .

Raman spectroscopy was also used to examine the chemical composition of features viewed in the SEM. The blue spectrum in the lower portion of Figure 5.38 is from the original untested material and shows that the ZrO_2 is in a tetragonal phase. This spectrum was taken with a 473 nm laser using a 1800 grating at 100x. The red spectrum in the upper portion of Figure 5.38 is from a single grain of ZrO_2 within the high deposition region shown in Figure 5.30b. The Raman spectrum matches that of a monoclinic phase ZrO_2 [125] and was taken with a 532 nm laser and 1800 grating at 100x. Tetragonal ZrO_2 phase was also observed by Raman in all other regions of the YSZ particles in tested samples except for the anomalous high deposition regions. The monoclinic phase would be thermodynamically stable below 500°C [97]. Below about 4 mol% $\text{YO}_{1.5}$, t- ZrO_2 transforms martensitically to m- ZrO_2 on cooling and back to t- ZrO_2 (also martensitically) on heating [92], [126]. If regions such as deposits have less than the initial 5.7 mol% yttria then they will be more susceptible to transformation to the monoclinic phase. This would explain the visual observation during testing that the large deposition regions begin forming before reaching steady-state temperature and could be transformed to the monoclinic phase during

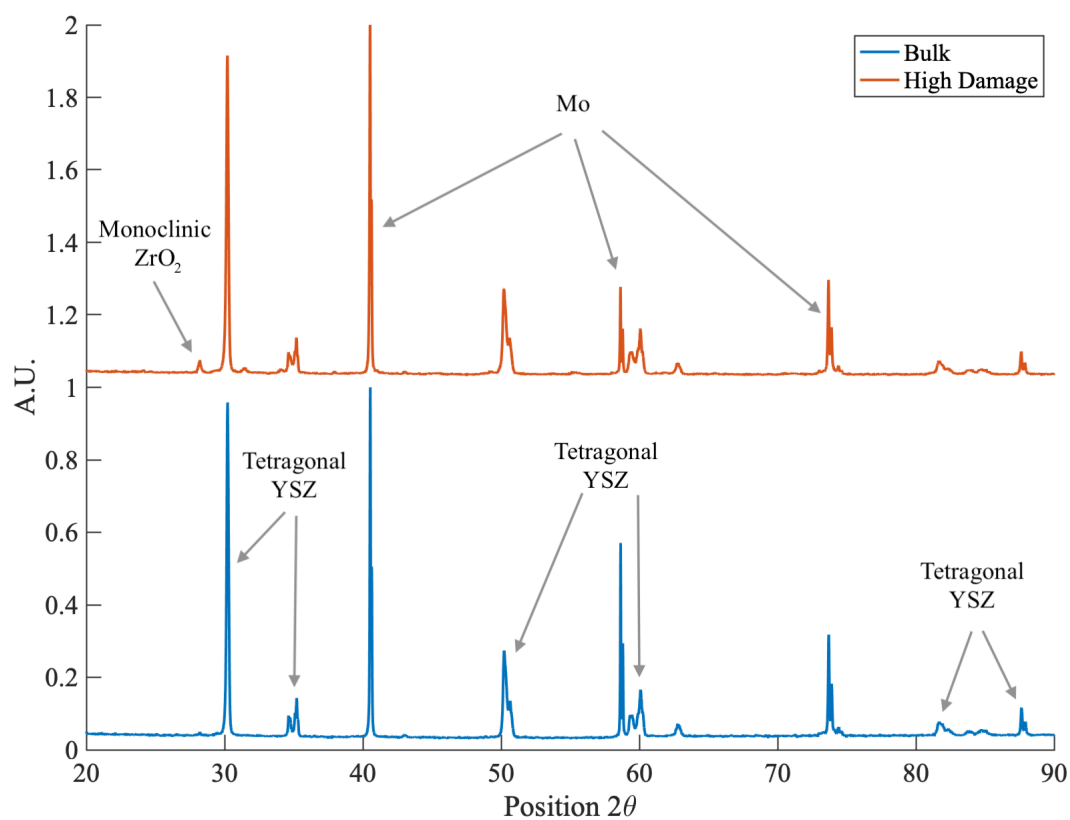


Figure 5.37: XRD spectra for a 60vol% Mo-YSZ cermet thermal cycled at 2000 K. The bulk data (blue) matches the peaks for pretest data. When centered on the intense deposition area (red) a new monoclinic peak appears at 28.2°

cool down. Deposited material may be more likely to transform as it is not mechanically constrained like the original YSZ spheres.

Following high temperature (2250–2630 K) testing in hydrogen, the YSZ grains experienced grain boundary erosion as well as some apparent surface debonding behavior and a distinct striation behavior (Fig. 5.33a–5.34). These laminations are predominantly parallel within a single grain and change direction in neighboring grains as viewed from the surface. The striations are visible under optical microscopy after even a single 20 min thermal cycle as shown in Figure 5.33b.

Some striations break the overall parallel trend and change direction near edges in a single grain. Striations are also visible in a SEM for both backscattered electron and secondary electron images in some regions. These striations did not appear in the 2000 K tests but did appear in 2250 K tests and above. The 2000 K specimen surfaces were not as well-polished as the specimens in subsequent tests, which many have obscured the effect. With higher temperature and higher mass loss there will be more surface vaporization which also may be important for promoting this behavior at higher temperatures. Alternatively, the striation mechanism may be temperature dependent with a threshold between 2000–2250 K. One explanation is that these striations may be caused by buckling due to uneven thermal expansion in the long crystal direction of the YSZ tetragonal structure.

The apparent debonding behavior from the Mo matrix as shown in Figure 5.33a–5.34 has been noted in samples tested at many temperatures. The YSZ is often at a slightly lower vertical height than the Mo matrix following high temperature testing, whereas prior to testing they are polished to the same level and is likely caused by the large difference in the thermal expansion coefficients for Mo and YSZ. This behavior motivated exploring the Mo-YSZ interface below the surface.

Focused ion beam milling was used to create a thin slice of the Mo-cermet thermally cycled four times at 2500 K. The dimensions of this lift-out section before additional thinning were approximately 15x10x2 μm . This sample was taken from a region with apparent debonding at the surface; significantly, the lift-out section shows that the debonding does not continue along the interface and is exclusively a near surface effect. The sample showed structural integrity through this extraction process, demonstrating that the sintered bond

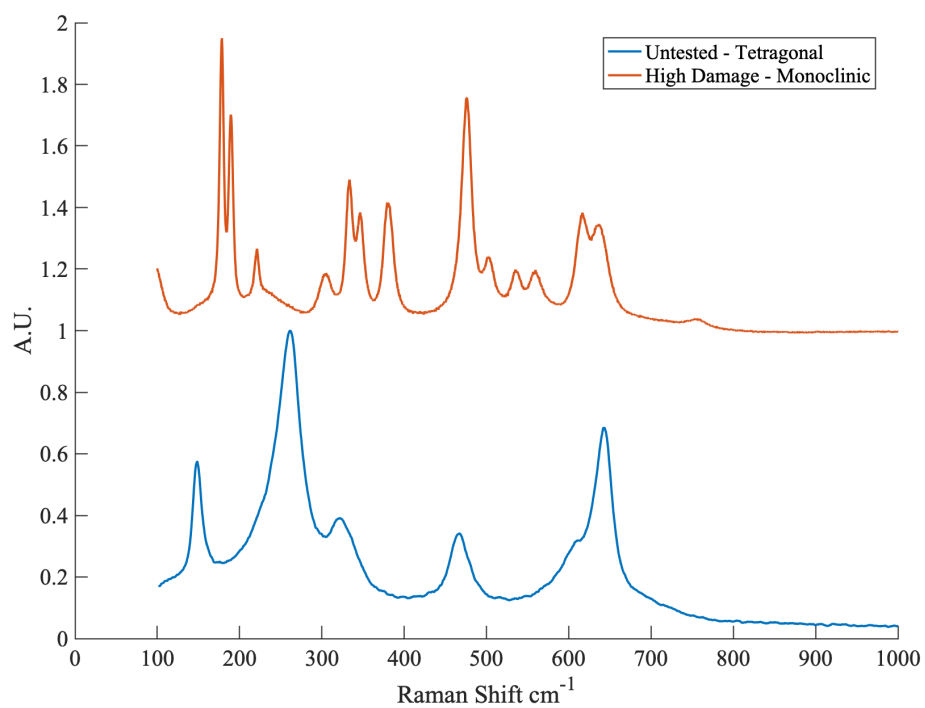


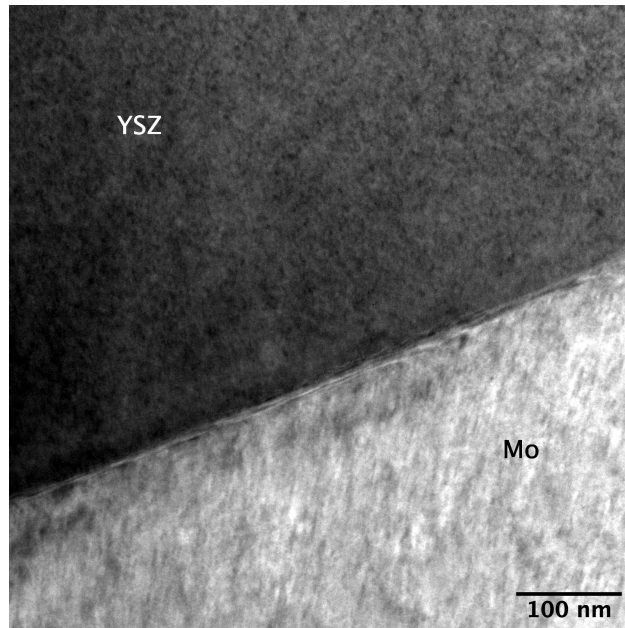
Figure 5.38: Raman spectra of untested cermet with tetragonal phase ZrO_2 (blue) and of a single ZrO_2 grain in the high damage region shown in Figure 5.30b with monoclinic phase (red)

at the interface remained strong even after thermal cycling and exposure to hydrogen. This is significant as the sample was taken from the hydrogen exposed surface of the material and not an interior position. This slice was then thinned with the FIB to a thickness of ~ 100 nm imaged with a transmission electron microscope. Figure 5.39a shows a TEM image along the interface between the Mo and YSZ. The TEM analysis along the full length of the interface region does not show evidence of cracking or secondary phase formation anywhere along the boundary.

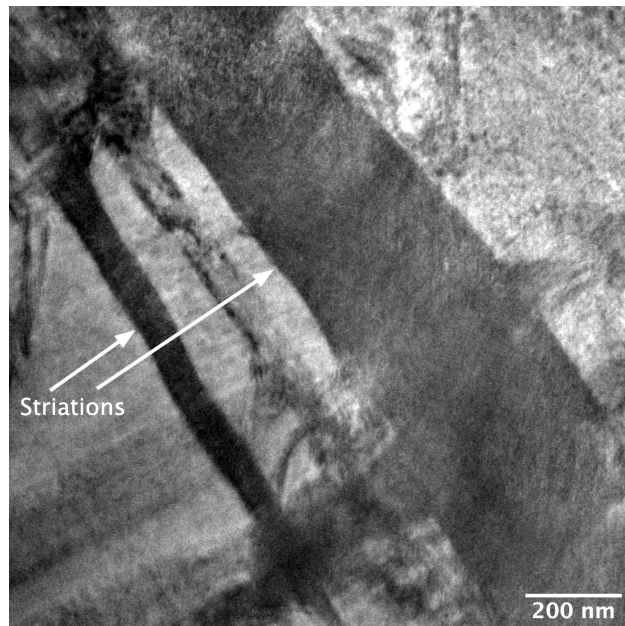
A second sample was prepared from the same material and the TEM image in Figure 5.39b shows the YSZ portion of this sample. These patterns in the YSZ may be the subsurface examples of the striations along the ceramic surface. However, it is notable they are not parallel below the surface.

An alternative explanation for the intricate subsurface behavior is the optical observation of discolored spots on the YSZ surface as shown in Figure 5.40a. These spots have brown and gray discoloration under optical microscopy. This spot-type behavior appears white in the BSE image in Figure 5.40b, just like the parallel striations. There is some evidence from surface Raman spectroscopy that the spots may be due to reduction of the YSZ during the hydrogen exposure.

A Raman spectrometer was used to observe both the spot-type areas and striation-type regions of the Mo-YSZ cermets. The striations did not show a substantial difference from the spectra of the surrounding area. This could be due to their small size as compared to the laser spot size of $2\text{ }\mu\text{m}$, or to minimal chemical and structural differences. However, the observation of the spot-type areas as shown in the spectra in Figure 5.41 showed both a significant reduction in Raman intensity as well as peak broadening and shifts. The intensity reduction could be caused by a variety of factors, such as surface roughness, or could indicate reduction of the ZrO_2 . The cubic-phase phonon peak from Pomfret[83] (617 cm^{-1}) appears as 645 cm^{-1} for the dark tetragonal regions of these samples. It is notable that this peak is down shifted to $\sim 590\text{ cm}^{-1}$ in the light-spot regions shown in Figure 5.41. This may indicate a loss of ZrO_2 relative to Y_2O_3 in the spot regions. However, not all of the spectra collected from spot regions show the peak shift away from 645 cm^{-1} . Other spectra maintain this peak while shifting those near 500 cm^{-1} as shown in Figure 5.42. This effect is not purely due to laser

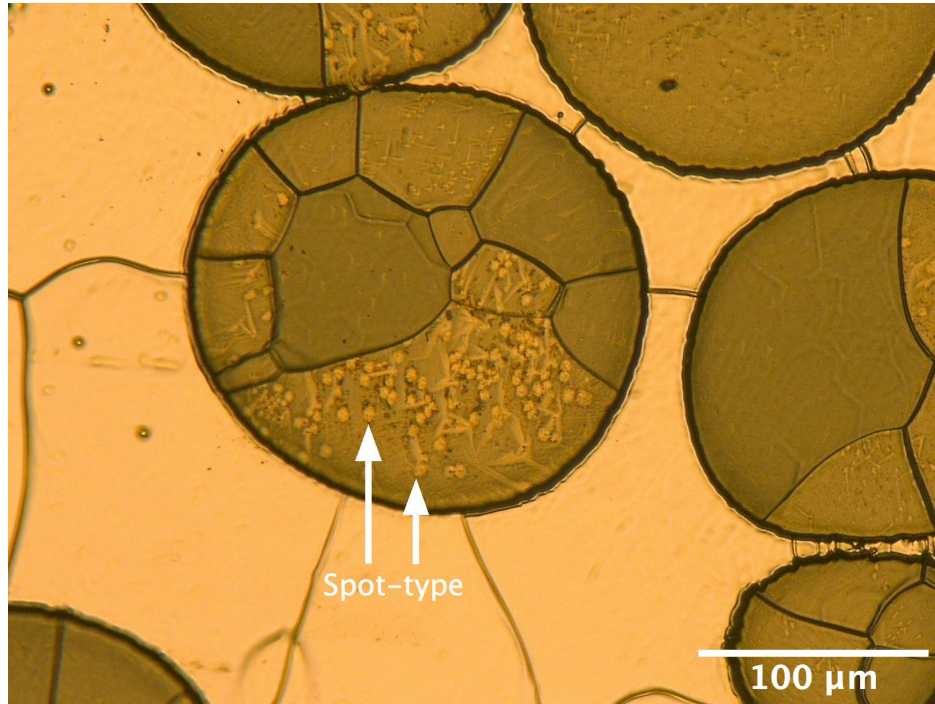


(a) Mo-50%YSZ cermet interface as observed by the TEM in bright field mode 2500K TC 50%. Bond is quite secure even after FIB liftout.

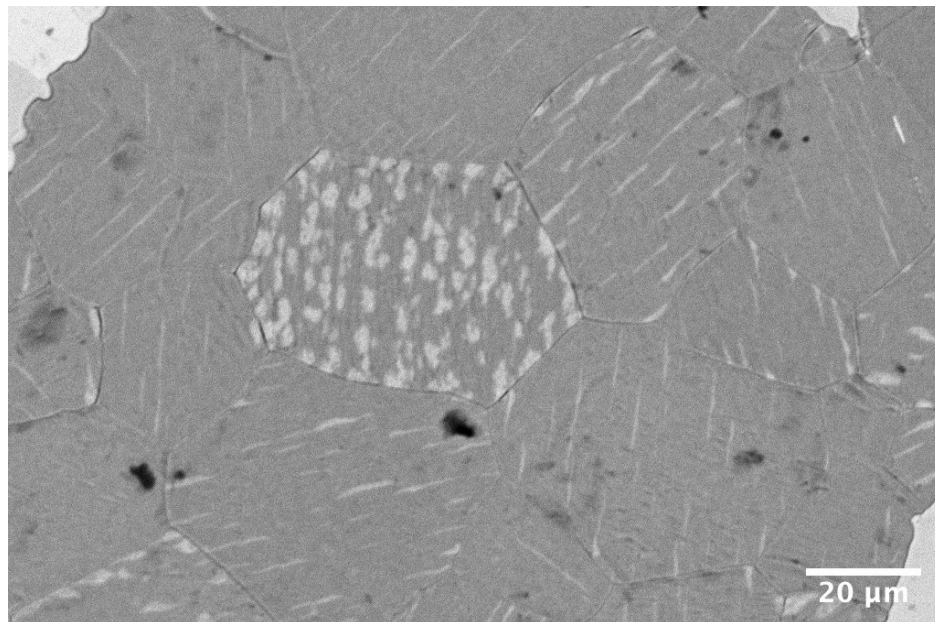


(b) Bright field TEM image of YSZ section highlighting the subsurface striations. 2500K TC.

Figure 5.39: TEM Images



(a) Optical image of Mo-60%YSZ cermet that shows the spot-type behavior in the YSZ. Tested with four thermal cycles at 2500 K.



(b) BSE image of Mo-60%YSZ cermet that shows both spot-type behavior in the central grain and striation-type behavior in the surrounding grains. Sample tested at SS at 2250 K.

Figure 5.40: Spot Images

wavelength as most spot regions show the shifts summarized in Figure 5.41 using both 532 and 473 nm wavelengths. Another possible explanation for either the striation or spot type behavior based on the YSZ phase diagram is the addition of a combined tetragonal+cubic phase, though the Raman and XRD measurements have not shown any definitive evidence for cubic phase.

5.3 Discussion

The Mo matrix exhibits good compatibility with flowing hydrogen up to 2630 K (0.91 T_M) as evidenced by acceptably small mass loss for the 80 minute exposures (both steady state and thermal cycled). Since the measured mass loss in the Mo-YSZ cermet increases with increasing vol% YSZ, YSZ appears to be providing most of the mass loss as compared to the Mo matrix. It was confirmed that the mass loss in pure Mo specimens is roughly equal to the slight sublimation of Mo at these flow rates (based on vapor pressure mass loss modeling, Eqn. 5.1 and Table 5.1). There is no evidence for any pronounced Mo-H chemical reactions up to 2630 K (0.91 T_M). Oxides in general are susceptible to reduction in hydrogen at high temperature. This is well documented for ZrO_2 [75] and also occurs in UO_2 , due in part to its large stable phase envelope of UO_{2-x} at high temperature[127].

Mass loss even for the highest test temperature of 2630 K is lower than or comparable to the historic peak mass loss rate experienced by the most successful test at the end of the Rover/NERVA program in the nuclear furnace which was 16.2 mg/cm²hr within the “mid-band corrosion” area in a 110 min test with an exit gas temperature of 2440 K[4]. The comparison to the nuclear furnace data is valuable as a benchmark even though it used a uranium carbide–zirconium carbide composite fuel and not a cermet–type monolithic particle fuel. Cermet were also researched in historic NTP programs; the best mass loss rates observed by Lenz et al. on Mo-20-25 vol% UO_2 cermet were 5–10 wt% at 2550 K for 30 min.[31] These Mo cermet were tested in flowing H_2 at 1 atm (flow rate not provided, but they claimed the UO_2 loss was consistent and not greatly affected by a 3x change in the H_2 flow rate)[31]. The 2800 K results at 10 min showed more than 17 wt% loss, and they state the UO_2 losses accelerate at 2700 K and at higher temperatures match the vapor

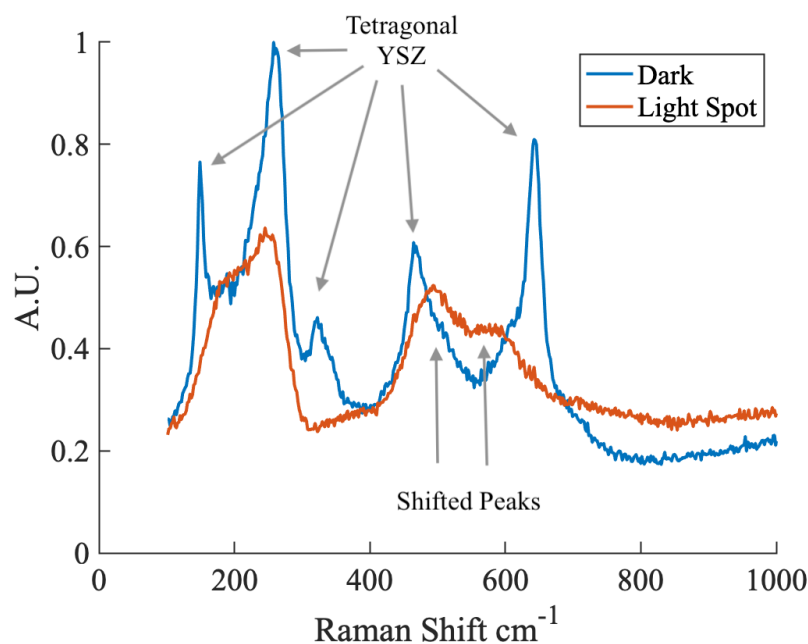


Figure 5.41: Blue: Spectra of typical dark region, very good match to expected tetragonal YSZ. Red: Light-colored spot region. Peaks shifting towards 500 and 590 cm^{-1} may indicate increased yttria content relative to zirconia content. Reduction in intensity may be indicative of hydrogen pickup. Taken with a 532 nm laser.

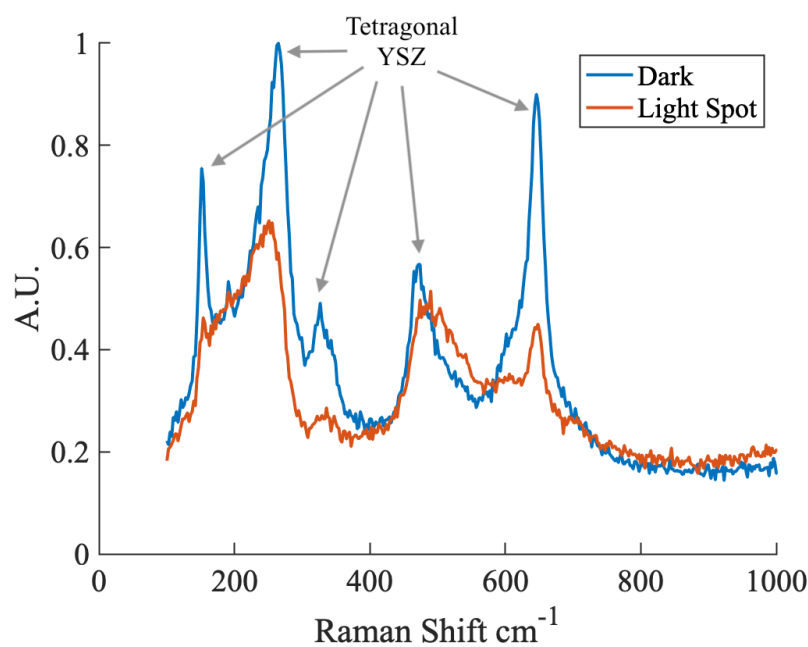


Figure 5.42: Blue: Spectra of typical dark region, matching expected tetragonal YSZ. Red: Light-colored spot region. Reduction of intensity still present, but all peaks are present and remain unshifted. Taken with a 473 nm laser.

pressure curve. The mass loss behavior as a function of time on different samples at 2550 K also appeared to be sub linear. They state that the losses in the first minutes of testing were from the outermost 25 μm layer.

The erosion along these grain boundaries throughout the sample suggest H_2 is fully penetrating the sample at 2500–2630 K. A simple estimate of hydrogen diffusion for these samples and temperatures using $x = \sqrt{DT}$ with a hydrogen diffusion coefficient in Mo extrapolated from lower temperature data[62], $D = 4.0 * 10^{-8} \exp \frac{-22.3 \text{ kJ/mol}}{RT} \left(\frac{\text{m}^2}{\text{s}} \right)$, shows that H_2 should diffuse through 3–4 mm of Mo for 20 min exposures at 2000–2500 K. Other diffusion coefficient values predict a H diffusion distance of 12 mm[121]. These values indicate that the entirety of the subscale samples used in this study should be exposed to the H_2 during the experiment across the entire temperature range.

These same hydrogen diffusion calculations for the YSZ particles have more mixed results, due to uncertainties in the hydrogen diffusion coefficients for tetragonal YSZ. Using the diffusion coefficient reported for a cubic-YSZ[122] a 20 min exposure at 2500 K could penetrate greater than 250 μm and therefore it is expected that the full YSZ particle would be exposed. However, for ZrO_2 oxides grown on various zirconium alloys the reported range of the H diffusion coefficients span several orders of magnitude[123], [124]. This same 20 min exposure at 2500 K can produce values from 5 μm up to 1mm depending on the starting Zr-based alloy. The interior YSZ cracking observations shown in Figure 5.23 suggest that the full YSZ particle is exposed to the hydrogen over the course of the four thermal cycles at 2500–2630 K. Similar analysis using the standard diffusion coefficient for H_2 in W [128] predicts a H range of 8mm. Prototypic NTP fuel designs such as the hexagonal fuel elements with 61 coolant channels in the SCCTE model[20], [21], [129] have approximately 1.1 mm of cermet between neighboring coolant channels with a 170 μm cladding on the coolant channel. Consequently, the high temperature regions in a prototypic NTP cermet fuel will also have deep H_2 penetration throughout the cermet matrix unless highly efficient H permeation barriers are deposited on all H-facing surfaces.

The mass loss results presented here on the Mo cermet containing surrogate YSZ particles are significantly better than recently reported testing of a Mo- UO_2 cermet with a single thermal cycle at 2500 K for 30 min [130]. The Mo- UO_2 sample exhibited extensive cracking

in both the Mo matrix and the UO_2 , significant swelling and mass loss of $3.59 \pm 0.15\%$ driven primarily by the loss of the UO_2 . The XRD analysis showed evidence of α -uranium as well as a $\text{U}_{0.88}\text{Mo}_{0.12}$ intermetallic phase. The presented micrographs showed some uranium visible in Mo grain boundaries. The sample was not thermal cycled, which would be expected to further exacerbate this behavior. The present study shows significantly better performance than the Mo- UO_2 cermet, with less than 1% mass loss shown for all Mo-YSZ samples up to 2630 K for longer exposure times (with and without thermal cycling) and no evidence of a similar metal loss mechanism such as free Zr in grain boundaries. The presence of yttria may have improved the performance of the YSZ surrogate material compared to the UO_2 particles with no additives. Historic research has shown that an oxide stabilizer in UO_2 (e.g. ThO_2 , Gd_2O_3 , Y_2O_3 , Ce_2O_3) at 5-10 mol% will improve the H corrosion performance of the cermet by making it more difficult for the UO_2 to become hypostoichiometric.[28] Although the primary reason for adding yttria to the zirconia surrogate was to produce YSZ with a stabilized tetragonal crystal structure (to avoid undesirable phase transformations during heating and cooling), the yttria may also be serving a beneficial role of acting as an oxide stabilizer to suppress loss of oxygen in ZrO_2 during high temperature hydrogen exposure.

Lenz measured UO_2 loss for (W/30 at.% Mo/12-17 %Re)–40 vol.% UO_2 cermets with and without additions of 4 vol.% Y_2O_3 to the fuel, following thermal cycling (30 min intervals) at 2875 K. The Y_2O_3 stabilized cermet clearly showed the least amount of UO_2 loss, with a reported loss of 0.5% (no unit). This was in contrast to cermets without the yttria additions to the fuel particles which had “essentially infinite mass loss” after several thermal cycles [131]. The Y_2O_3 was described as stabilizing the UO_2 from the loss of oxygen by either 1) lowering the partial molar free energy of oxygen in the ceramic phase without the possibility of forming free metal on cooling or (2) with the addition of Y_2O_3 , the uranium in UO_2 is transformed to the hexavalent state, which does not reduce to U metal. UO_2 can maintain an oxygen-to-metal ratio of 2.0 to 2.1 with additions of rare earth oxides by forming a defect lattice structure[132]. Future testing with Mo- UO_2 cermets should include a stabilizer in the UO_2 such as yttria or other oxides used in previous development programs.

Benensky et. al. found that CVD SiC tested at similar H_2 flow rates (12 cm/s) and pressures (1 atm) with 4 thermal cycles of 30 min could only be used as an NTP fuel material

(without use of a protective corrosion cladding/coating) at temperatures up to 2000 K since its mass loss rate during exposure to flowing hydrogen at 2000 K exhibited linear kinetics with a rate of 2.6 mg/cm²hr (8.1 μ m/hr uniform erosion rate). The corresponding mass loss rate at 2250 K increased by nearly one order of magnitude to 21 mg/cm²hr, (65.4 μ m/hr uniform erosion rate)[133]. The SiC volatilization rate was observed to be proportional to the $\frac{1}{2}$ power of H₂ gas flow rate. Typical proposed NTP flow rates and pressures are 12.5–34 kg/s and 2.8–6.9 MPa depending on engine thrust level[41,42] which are much higher than the pressure (0.10 MPa) and flow rates (7.4×10^{-7} kg/s) of the subscale facilities used in this study. Using these mass flow rates and a cross-sectional flow area with the SCCTE dimensions, a prototypic system would have a flow velocity of 49 m/s compared to the 12 cm/s in this study. While the mass loss scaling factor with flow rate is not known for cermets, if it is a $\frac{1}{2}$ power like SiC then at prototypic flow rates Mo-cermets at 2500 K for 80 min would scale from 9-12 mg/cm² to 620-765 mg/cm². However, since the mass loss is sublinear with respect to time ($\frac{1}{3}$ or $\frac{1}{2}$ power) unlike the linearly dependent SiC, it is likely this simple analysis may provide a significant overestimate. Further testing on varying mass flow rates are needed to provide improved insight.

Based on cross-section microstructural analysis (e.g., Fig. 5.35), the observed Mo-YSZ particle interface separation at the surface of samples following high temperature hydrogen exposure is simply a near-surface phenomenon. The depth from the surface where separation between the Mo matrix and the YSZ particle occurred was typically less than 1-2 μ m but could be up to 20 μ m for 70% samples at 2630K; in any case, the separation depth is a small fraction of the particle diameter, and in actual NTP fuel systems the material exposed to the hot flowing hydrogen would be either the metal matrix (without any fuel particles) or more likely a hydrogen permeation barrier cladding. The observed Mo-YSZ particle surface separation is due in part to uneven erosion during polishing, thermal stress from CTE mismatch during high temperature testing and cooldown, and different erosion rates in the H₂ environment between the Mo and YSZ. The particle-matrix interface retained strong bonding beneath the surface as shown by the subsurface TEM characterization as shown in Figure 5.39a. Cermets are prone to CTE mismatch that can cause high stress and lead to debonding between the Mo matrix and the YSZ particles. This can be of particular concern

under high thermal gradients and neutron irradiation. A one-dimensional approximation of this thermal stress can be calculated based on the difference in coefficients of thermal expansion of the Mo and YSZ, $\sigma = E_{YSZ} (\alpha_{YSZ} - \alpha_{Mo}) \Delta T$. Assuming the interface strain is zero in the as-sintered cermet condition at 1673 K, the resultant compressive stress in the YSZ particles is estimated to be on the order of 600 MPa at 2500 K. More importantly, the tensile stress that develops at the Mo/YSZ interface during cooling down to room temperature from the high temperature hydrogen testing temperature (if one assumes thermal creep rapidly relaxes the tensile stress in the Mo matrix at these temperatures that approach 86–91% of the absolute melting temperature of Mo) is on the order of 1.4–1.9 GPa following testing in the temperature range of 2000–2630 K. These approximations are done using the thermal expansion coefficient (α) of 6.5 $\mu\text{m}/(\text{m K})$ for Mo and 10.5 $\mu\text{m}/(\text{m K})$ for YSZ and an elastic modulus of 329 GPa for Mo and 200 GPa for YSZ. These values are extrapolated from lower temperature data (valid up to 1000 K). This stress may contribute to the internal YSZ cracking observed in the cross-sectioned samples thermal cycled at 2500–2630 K shown in Figure 5.22.

It is possible that the hydrogen attack of the YSZ grain boundaries is due to the reduction reaction of H on ZrO_2 and producing H_2O vapor as predicted by Gibb’s free energy calculations (Fig. 3.1). Another potential factor is the potential interaction with aluminum oxide which is present in small amounts in the YSZ (0.25 wt%). The Al_2O_3 is likely used as a sintering aid and would preferentially be found along the YSZ grain boundaries and so the aluminum oxide may be where the reduction and gas formation is preferentially taking place. This reaction also explains the difference in YSZ grain size in the attacked interior from that at the surface. Grain growth is likely inhibited once there is enough buildup of gaseous species along the grain boundaries beginning between 2250–2500 K which leads to a maintaining a smaller grain size even at high temperature. At the surface, the diffusion path for these gaseous species is much shorter and no gas bubble buildup is observed; consequentially larger grain sizes occur since there is no grain boundary pinning by gas bubbles.

A key failure mechanism in historic cermet fuel tests is the loss of the fissile fuel [40]. Fuel on the surface is preferentially lost by high temperature vaporization of UO_2 . Interior

(bulk) UO_2 fuel is lost due to reduction of UO_2 to sub-stoichiometric UO_{2-x} at temperatures exceeding 1670 K (temperature where the UO_{2-x} envelope opens in the phase diagram[134]) and subsequent migration of free uranium (U) and oxygen (O) products by grain boundary diffusion. In the reducing hydrogen environment, the H_w can penetrate the cermet by grain boundary and metal matrix diffusion. During cooling, free U can then react with O in grain boundaries to reform UO_2 or in a subsequent thermal cycle can react with hydrogen to form UH_3 . Volume changes associated with these processes weaken the metal matrix mechanical integrity by intragranular cracking and can eventually induce structural failure of the cermets.[40] This behavior is significantly worse if the UO_2 is interconnected or if there are cracks or pores in the metal matrix. The loss of metal due to vaporization at high temperatures has not been a historic concern for W cermets as W has a significantly lower vapor pressure, but needs to be investigated with Mo cermet alternatives.[50] Other behaviors leading to fuel failure are the mismatch of thermal expansion coefficients of the ceramic fuel and the metal matrix which can lead to cracking.[40] Surface coatings may be applied to H_2 flow channels to suppress the undesirable corrosion reactions with hydrogen; however, it is desirable for the fuel to have at least moderate compatibility with H_2 at high temperature to avoid catastrophic degradation if coatings are breached. Additionally, creating coatings that are impermeable to H_2 that are <1 mm thick at these temperatures is unlikely.

The Gibb's free energy calculations from Figure 3.3 indicate that UN may have even greater phase decomposition issues than what has been experienced by UO_2 in cermets. UN has a U gaseous phase concentration an order of magnitude higher than UO_2 at the same temperatures and the liquid U phase is 3 orders of magnitude higher than the gaseous U value from UO_2 . Therefore, uranium diffusion into grain boundaries should be more problematic for UN cermets than for UO_2 cermets.

Recent results from cermet studies performed with both UO_2 and UN show significant diffusion of uranium into the metal matrix [130], [135]. These experiments examined a Mo- UO_2 cermet with a single thermal cycle at 2500 K for 30 min[130] and a W/Mo-UN fuel element with a single thermal cycle at 2250 K for 20 min[135]. In the current work there has been no evidence of Zr or Y metal diffusion; i.e., the YSZ behavior appears to

be dissimilar to what is observed for the uranium compounds. However, historic cermet development programs for NTP used oxide additives (e.g. ThO_2 , Gd_2O_3 , Y_2O_3 , Ce_2O_3) to the UO_2 to help maintain oxygen in the system[40], [48], [131], [132]. These oxides were described as stabilizing the UO_2 from the loss of oxygen by one of two potential mechanisms 1) the oxide additive lowers the partial molar free energy of oxygen in the ceramic phase without the possibility of forming free metal on cooling or (2) with the addition of oxide, U is transformed to the hexavalent state, which does not reduce to U metal. UO_2 can maintain an oxygen-to-metal ratio of 2.0 to 2.1 with additions of rare earth oxides by forming a defect lattice structure[132]. Future testing with Mo- UO_2 cermets should include a stabilizer in the UO_2 such as yttria or other oxides used in previous development programs.

Regarding the use of YSZ as a surrogate for UO_2/UN at high temperature, it is important to be aware of the martensitic transformation to the monoclinic phase at low temperatures that may occur during cool down. These phase changes may be affecting the mechanical stress of the system. To help prevent the phase change, this may warrant utilizing more yttria in the system to fully stabilize the cubic crystal structure, which is more similar to UO_2 anyway. Al_2O_3 as an impurity (sintering aid) makes YSZ worse for high temperature H_2 applications and should be limited if possible. For a UO_2 system, particularly if it is a mixed oxide to help stabilize the UO_2 , the amount of Al_2O_3 should be limited to a low volume fraction in the fuel specification. If stabilizing oxides are selected for addition to UO_2 in NTP systems, then thermodynamic calculations should be performed with the proposed system to eliminate choices that would increase vaporization.

Based on the mass loss data and vapor pressure calculations, the Mo matrix erosion rate appears to be small at 2500 K (0.7–1.3 mg/cm²hr based on volume loading) and is higher at 2630 K (2.8–5.6 mg/cm²hr based on volume loading). The Mo matrix demonstrates robust behavior as evidenced by no observation of matrix cracking under any condition. The YSZ erosion rate (vaporization and H_2 corrosion) also appears acceptable up to 2630 K (on the order of 10–15 mg/cm² for 80 min tests). However, there are some concerns shown by the cracking of the YSZ particles along the grain boundaries in the interior of the cermet sample, some evidence of gas bubble formation and some Mo/YSZ interface debonding at the surface. With the sublinear mass loss behavior on the order of $\frac{1}{3}$ to $\frac{1}{2}$ power with time and low mass

loss rate after the 1st thermal cycle, Mo-YSZ cermets perform well under NTP conditions up to at least 2630 K. However, the link between the surrogate YSZ corrosion to that of actual UO_2 , or UN particle fuels is unclear. Gibb's free energy minimization calculations suggest that UN has a U gaseous phase concentration an order of magnitude higher than UO_2 at the same temperatures and the liquid U phase in UN is 3 orders of magnitude higher than the gaseous U value from UO_2 . Therefore, uranium diffusion into grain boundaries should be even more problematic for UN cermets than for UO_2 cermets. Without a hydrogen permeation barrier, the nuclear fuel would likely experience strong attack and could be problematic for an NTP system. Therefore, future research into the compatibility of hot hydrogen with Mo-(UO_2 or UN) cermets (including doping with yttria and other H corrosion-stabilizing additives) is needed.

For future testing of cermets for NTP care must be taken with the assumption of H_2 diffusion distance. As shown in this work, at NTP relevant temperatures the H_2 can easily diffuse through more Mo matrix than is present between fuel channels. Since there will be great penetration of the H_2 through the metallic matrix the fuel will need to be designed to operate in the H_2 environment. The Gibb's free energy calculations suggest that UO_2 will be more resistant to the H_2 corrosion than UN. The historic literature suggest that adding an oxide stabilizer to the UO_2 will greatly improve its behavior when exposed to H_2 .

As the mixed oxide seems to be important to improve the performance of the UO_2 , thermodynamic studies should be done to evaluate which would have the least corrosion under H_2 . This is an important first step as this study showed that the addition of Al_2O_3 to the YSZ created increased interactions with the H_2 . The oxides highlighted in the historic testing such as ThO_2 , Gd_2O_3 , Y_2O_3 , Ce_2O_3 are the likely candidates to be used as additives.

An ideal future experiment would obtain 200 μm UO_2 spheres with 3–10 mol% additive oxide (ThO_2 , Y_2O_3 or Ce_2O_3) incorporated into the fuel. These would then be sintered with Mo powder or a MoW alloy powder (Mo with 30 wt% W) with 60 vol% UO_2 fuel. After the carbide reaction layer was removed by polishing additional powder could be added with another sintering step to create a Mo cladding with 400–500 μm thickness so that the Mo carbide reaction layer could again be polished off and the sample would retain the desired 200 μm Mo coating. These samples could then be thermal cycled in either the CFEET or

BWXT furnaces and would give very applicable mass loss results and corrosion behaviors for the NTP system. These results would also be enhanced by varying the flow rate in the furnace so that a mass loss to flow rate function could be defined for the ideal UO_2 + additive oxide fuel that could scale to the flow rates expected in a full scale NTP prototype.

Chapter 6

Conclusions

The molybdenum samples showed minimal mass loss up to 2630 K in a hydrogen atmosphere; the observed mass loss at 2630 K was 40% lower than the vapor pressure predictions at low flow rates. This indicates that H corrosion of Mo is minimal up to temperatures 91% of the absolute melting temperature of Mo. This supports the use of Mo as a candidate structural material for nuclear thermal propulsion applications. Pronounced grain growth was experienced during high temperature exposures for 80 minutes with a grain growth activation energy of 160 kJ/mol. Striations that aligned with crystal direction were observed and attributed to pileup of monoatomic ledges.

Mo-YSZ cermet wafers with 40–70 vol% ceramic loading were observed to exhibit good stability during flowing H₂ testing under steady state and thermal cycling conditions for temperatures between 2000–2630 K for up to 80 minutes with sublinear mass loss rates with time ($\frac{1}{3} - \frac{1}{2}$ power) and low total mass loss (<1 wt%). The promising behavior with a surrogate fuel motivates future testing on Mo-UO₂ and Mo-UN cermets. Localized areas of both Mo and Zr-rich deposits have been observed on the surface after testing; however, these are likely an artifact from the gas flow path in the testing apparatus and should have minimal impact in a prototypic NTP system. Mass loss results show that these Mo-YSZ cermets exhibit much lower hydrogen corrosion mass loss rates than SiC and graphite matrix fuels at NTP-relevant exposure temperatures, and perform similarly or superior to historic Mo/W-UO₂ cermets. The observed YSZ-Mo interfacial debonding at the sample surface for the highest investigated test temperatures is a localized near-surface phenomenon and

this debonding is not observed in subsurface particles. From diffusion estimates H_2 will be fully penetrating the samples during testing at NTP-relevant conditions and therefore adequate chemical compatibility of the subsurface fuel particles with hydrogen is essential. Significant cracking of the YSZ particles occurred in the interior of cermet samples at 2500–2600 K, though no Mo cracking was observed and a strong YSZ-Mo bond was still present. A hydrogen corrosion stabilizer (such as Y_2O_3) is likely needed for UO_2 fuel kernels to achieve low mass loss during exposure of cermet fuels to flowing high temperature hydrogen. Raman spectroscopy and XRD show evidence for a phase change in the YSZ from tetragonal to monoclinic where yttria content becomes low. There was evidence for significant hydrogen attack at grain boundaries of the YSZ throughout the interior of the sample likely enhanced by the presence of the alumina impurity. As a surrogate material for UO_2/UN , using higher yttria content may help reduce the phase changes to monoclinic that happen during cooling and alumina content should be reduced if possible.

Based on the thermodynamic data future cermet testing may want to emphasize UO_2 testing over UN. Future experiments should prioritize obtaining UO_2 with 3–10 mol% additive oxide for cermet testing. Additionally, the mass loss data would be enhanced by varying the flow velocity in the furnaces to allow for better scaling of the mass loss results to NTP conditions.

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Vita

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