

**Evaluation of the Hydrothermal Corrosion of SiC and the Viability
of Mitigation Coatings to Protect SiC Across Typical LWR
Chemistry and Temperature Regimes**

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Abstract

An important challenge in the development of ceramic matrix composite SiC for accident tolerant fuel cladding applications is corrosion under normal operating conditions. The present study has investigated the chemical kinetics of chemical vapor deposited SiC with and without neutron irradiation. Four commercial coating varieties (physical vapor deposited TiN, CrN, Cr, and multilayer Cr/CrN) were deposited on CVD SiC as potential corrosion-mitigation coatings and examined in parallel with uncoated SiC. Samples were exposed to high purity compressed water between 288 and 350°C with 1-4wppm added O₂ or 0.15-3wppm H₂. Additionally, samples were exposed in the MIT Nuclear Reactor PWR-simulating water loop at 300°C in three locations corresponding to neutron damage with radiolysis, reduced radiolysis, and pure water only. The coatings were also exposed to radiation damage in Ar.

Pure, high resistivity CVD SiC was found to corrode in the active regime (no passivating SiO₂ film is formed). The reaction kinetics of CVD SiC was estimated to corrode with activation energy of 61 kJ/mol and 106 kJ/mol and a standard entropy of activation of -240 kJ/mol and -27 kJ/mol, with respect to water and aqueous oxygen, respectively. The overall corrosion rate in

mg/cm²s can be described by, $\text{Rate} = \frac{0.1458}{1+SA} T \left(1.09(1 - 10^{-3}T)[O_2]e^{-\frac{1.275 \times 10^4}{T}} + 7.91 \times 10^{-6}e^{-\frac{7.39 \times 10^3}{T}} \right)$, with T in kelvin and [O₂] in wppm. Polishing was found to have a significant effect on the observed corrosion rate in oxygen. Radiation fields increased the corrosion of SiC mildly and high resistivity SiC is predicted to recede less than 4µm in 5 years.

The coatings investigated in this work were not protective. TiN oxidizes and spalls, possibly due to interface destabilization. This was exacerbated by radiation damage and radiolysis products. The multilayer Cr/CrN cracked under irradiation in Ar and spalled in the presence of water. A monolithic CrN coating was more protective in the absence of irradiation and cracked less under irradiation in Ar. Cr was protective in deoxygenated conditions but quickly oxidized and subsequently spalled in the presence of oxygen. Radiation damage caused extensive cracking and ~0.2% void swelling in the Cr coating. More compressive residual stresses, higher purity, and higher coating ductility are recommended for future coating generations.

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List of Abbreviations

AFM	Atomic Force Microscopy
ATF	Accident Tolerant Fuel(s)
BDB	Beyond-Design-Basis
BWR	Boiling Water Reactor
BWR-HWC	BWR-Hydrogen Water Chemistry
BWR-NWC	BWR-Normal Water Chemistry
CMC	Ceramic Matrix Composite
CST	Corrosion Science and Technology
CVD	Chemical Vapor Deposition
CVI	Chemical Vapor Infiltration
DPA (dpa)	Displacements Per Atom
EBSD	Electron Backscatter Diffraction
EDS	Energy Dispersive Spectroscopy
FEA	Finite Element Analysis
GE	General Electric
HCL	Hydrothermal Corrosion Laboratory
HP	Hot Pressing
HR	High Resistivity
HTML	High Temperature Materials Laboratory at ORNL
HYCO	Hybrid Composites
ICSD	Inorganic Crystal Structure Database
JIAM	Joint Institute for Advanced Materials
LAMDA	Low Activation Materials Design and Analysis Laboratory
LOCA	Loss-of-Coolant Accident
LPS	Liquid Phase Sintering
LR	Low Resistivity
LWR	Light Water Reactor
MATLAB	Matrix Laboratory Program
MD	Molecular Dynamics
MI	Melt Infiltration
MIT	Massachusetts Institute of Technology
MITR	MIT Nuclear Reactor Laboratory
ML	Multi-layered
MTS	Methyltrichlorosilane
NEO	Neo Industries
NGNP	Next Generation Nuclear Plant Industry Alliance Limited
NITE	Nano-Infiltration and Transient Eutectic-Phase
OB	Oerlikon Balzers Coatings

ORNL	Oak Ridge National Laboratory
PHMS	polyhydromethylsiloxane
PIP	Polymer Infiltration and Pyrolysis
PKA	Primary Knock-on Atom
PWR	Pressurized Water Reactor
PyC	Pyrolytic Carbon
R&H	Rohm and Haas
RB	Reaction Bonding (same as RS)
RP	Richter Precision
RS	Reaction Sintering (same as RB)
SCRAM	Safety Control Rod Axe Man
SEM	Scanning Electron Microscopy
SHE	Standard Hydrogen Electrode
SREA	Surface Reactant Equi-density Approximation
TEM	Transmission Electron Microscopy
TKD	Transmission Kikuchi Diffraction
TM	Tech Metal
TMI	Three Mile Island
TST	Transition State Theory
UW	University Wafer

Chapter 1: Introduction

1.1 Fuel Safety Concerns in Light Water Reactors (LWRs)

Since the 1960's, considerable improvement has been made in the safety of LWRs, yet a key concern that remains is the stability of the fuel in the case of a loss-of-coolant accident (LOCA) or a beyond-design-basis (BDB) accident [1-3]. In order to avoid fuel meltdown or loss of fuel containment from the fuel rods during such events, it is desirable that fuel cladding possess the following characteristics [4-7].

1. Impermeability of cladding to fission gases
2. High mechanical strength, melting temperature, and thermal conductivity
3. Chemical compatibility with the coolant and fuel
4. Resistance to degradation from pellet-cladding interaction
5. Low neutron absorption cross-section
6. High radiation resistance
7. Isotropic properties (i.e., cubic lattice)

1.2 LOCA Corrosion Behavior of Zirconium Cladding

While Zr-based alloys perform adequately under standard operational conditions, when coolant to the core is lost, they pose a significant safety risk to the plant and surrounding region. At Three-Mile Island (TMI) in 1979, the combination of design, human, and mechanical errors led to the worst nuclear accident in the United States [3]. The reactor experienced a LOCA event following control rod insertion to kill operation (SCRAM). Because the fission process produces a series of decay products with very short to very long half-lives, a large amount of energy is still deposited into the core following SCRAM. This is equal to about 7% of full power immediately after SCRAM, 1% a few hours later, and 0.2% after several days [1]. This level of heating is significant and caused the core temperature to rise by several hundred degrees. As Zr-based claddings reach temperatures approaching 1200°C, the corrosion rate accelerates exponentially [5, 8, 9], and near 1200°C, the energy deposited from oxidation is larger than the decay heat energy, leading to breakaway oxidation [1, 6] as shown below in Figure 1.1. This process generated hydrogen (from the reaction of water) which at TMI was safely removed. At the Fukushima plant in 2011, it was the cause of the explosions which released radioactivity [2, 6].

To continue service in LWRs with the necessary safety specifications for BDB accidents, Zr-based claddings will need either extensive alloy modification, or adherent and self-healing oxidation-resistant coatings. Alternatively, new claddings are being researched including, Fe-based claddings which have superior mechanical and corrosion-resistant properties to Zr. However, these Fe alloys have significantly higher neutron absorption cross sections, and some cracking concerns [9]. Some refractory alloys have been tested, but these have, at best, only short-term oxidation resistance in steam. Finally SiC has certain attractive properties as a cladding possibility, including very low neutron absorption cross section and excellent high temperature oxidation resistance, but requires substantial engineering innovations for nuclear-

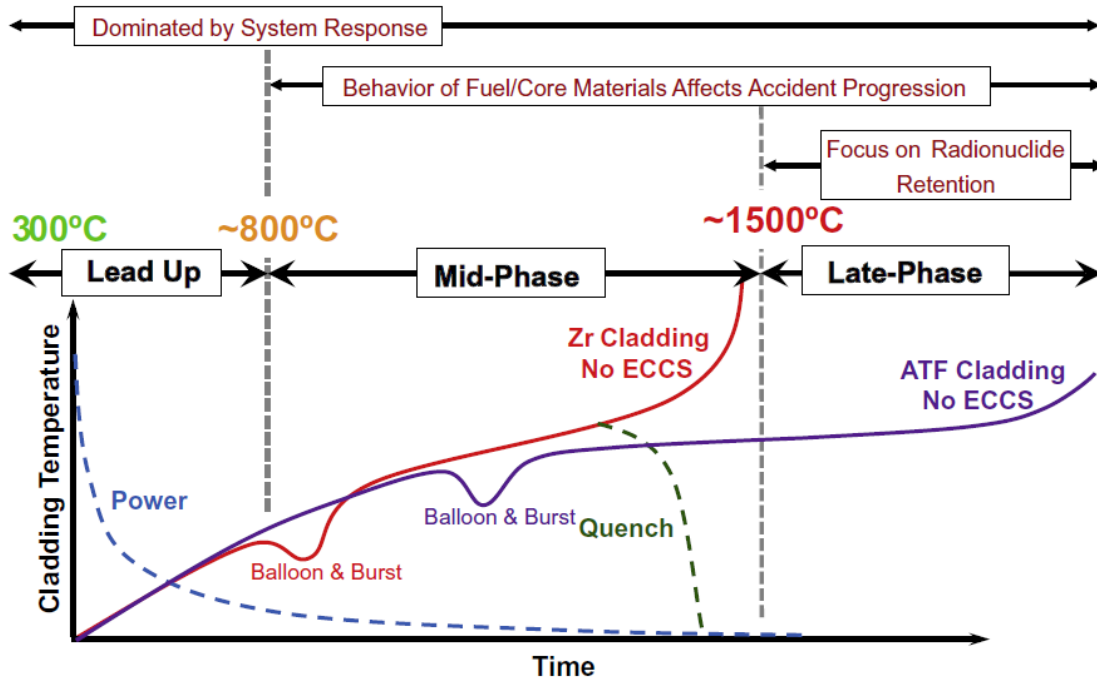


Figure 1.1: Response of a LWR reactor core to a LOCA accident scenario with and without ATF cladding. Reprint from the Journal of Nuclear Materials, 448, S.J. Zinkle, K.A. Terrani, J.C. Gehin, L.L. Snead, Accident tolerant fuels for LWRs: A perspective, 374-379, Copyright 2019, with permission from Elsevier.[1].

grade production and testing [1, 10-12].

1.3 Objectives of this Work

SiC has been investigated over the past several decades for use primarily in fusion and Generation IV fission nuclear reactors. Currently, SiC's excellent radiation stability, mechanical properties (when made as a ceramic matrix composite (CMC), thermal conductivity, and hermeticity of high density SiC make it a leading candidate for various structural materials. As such, it is attractive to consider SiC as a replacement to the Zr-based alloys for risk minimization. Several studies have shown that SiC will corrode quickly enough to cast doubt on its use in LWRs (see section 2.9). However accurate scientific kinetics have not yet been established. Therefore, this study aims to understand the corrosion mechanisms of SiC with and without mitigation coatings in liquid water up to 350°C and how these mechanisms are changed by radiation.

Chapter 2: Literature Review

2.1 Concepts in Accident-Tolerant Fuels

One of the significant remaining challenges associated with Zr-based cladding involves its performance under LOCA conditions; the decay heat generated during a LOCA is sufficient to cause breakaway oxidation of Zr-based cladding [1]. Safety systems are designed to mitigate this threat in all accident scenarios, and accident-tolerant fuels (ATFs) can help provide an additional layer of safety. In an accident, fuel failure is caused by initial boil-off of coolant by decay heat, dramatic increase in the fuel temperature due to lack of cooling, and subsequent oxidation and pin rupture. ATF cladding will need 1), better oxidation resistance than Zr-based cladding in steam, 2) good dimensional stability, 3) fission product retention at high temperatures (minimal balloon and burst likelihood), 4) ability to cope with pellet-cladding interactions, and 5) similar/better performance than Zr alloy cladding under normal operational conditions. Example operating conditions for PWRs are given in Table 2.1.

Several options for ATF cladding have been proposed. FeCrAl alloys possess some of the highest potential due to exceptional materials properties, and good corrosion characteristics under operating and accident conditions, with a downside of having increased neutron absorption [5, 6, 9, 13]. Under normal operating conditions, FeCrAl forms a chromia scale that passivates it, leading to very little loss of cladding. At high (accident) temperatures, chromia becomes unstable, and is replaced by an alumina scale which protects it until the temperature is reduced, at which point the alumina dissolves and is replaced again by chromia [10, 13-16]. FeCrAl coatings have also been applied to standard Zr-based claddings as a way to solve the corrosion issue, without substantially increasing neutron absorption. This approach suffers from the spallation, impact-removal, and erosion concerns generally associated with coatings, as well as inter-diffusion between the phases, requiring an intermediate layer of Mo or another diffusion barrier [9]. Mo claddings have recently been shown to possess acceptable short-term resistance to corrosion under steam [17]. Similarly, MAX phase alloys have been considered for their mechanical and corrosion resistant properties, however significant work must be done before MAX phases will be available for manufacture [10, 18].

Cr coatings on Zr-based clads have demonstrated marked improvement over simple Zircaloy, but have not yet been tested to high temperatures where Cr_2O_3 degrades [5]. Zr or FeCrAl-coated Mo claddings have also been preliminarily shown to have viable corrosion rates under LOCA conditions, and its high temperature strength would aid with retention of fuel through an accident [5, 6]. However, it also has a higher neutron absorption cross-section than Zr. A summary of the corrosion rates of various ATF materials and zircaloy-4 is provided below in Figure 2.1, from Pint et al., [10]. Under accident conditions, any of the listed materials, SiC, FeCrAl, Ti_2AlC , or SS would behave as desired. SiC has been proposed both as a coating on Zr-alloys [19], and in composite form as a stand-alone cladding. In the remainder of this chapter, the dependencies on the properties of SiC and its composite forms are summarized from the literature.

Table 2.1: Expected operating conditions of a PWR, based on the AP1000 design. Reprinted from the Journal of Nuclear Materials, 466, J.G. Stone, R. Schleicher, C.P. Deck, G.M. Jacobsen, H.E. Khalifa, C.A. Back, Stress analysis and probabilistic assessment of multi-layer SiC-based accident tolerant nuclear fuel cladding, 682-697, Copyright 2015, with permission from Elsevier. [20].

	0-18 months	18-36 months	36-54 months
Linear heating rate (kW/m)	36.1-32.7	32.7-29.3	29.3-25.9
Operating internal pressure (MPa)	1-7.33	7.33-13.67	13.67-20
Shutdown internal pressure (MPa)	5.6	11.2	16.8
Irradiation damage in displacements per atom, (dpa)	0-2	2-4	4-6
Heat transfer coefficient (W/m ² -K)	10,000	10,000	10,000
Operating coolant temperature (°C)	316	316	316
Operating coolant pressure (MPa)	15	15	15
Cladding shutdown temperature (°C)	50	50	50

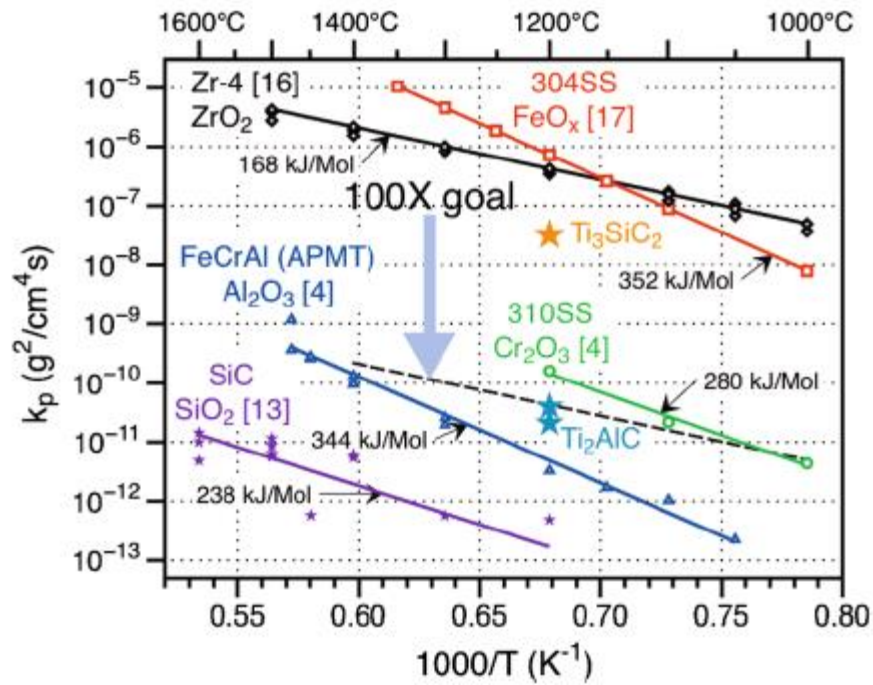


Figure 2.1: Arrhenius plot of the corrosion rate of various ATF-candidate cladding materials. Reprinted by permission from Springer Nature, Metallurgical and Materials Transactions E, Material Selection for Accident Tolerant Fuel Cladding, B.A. Pint, K.A. Terrani, Y. Yamamoto, L.L. Snead, Copyright 2015 [10].

2.2 Processing Variants of SiC

This section describes how typical variants of SiC are made as well as some of the processing trade-offs that must be considered in engineering applications.

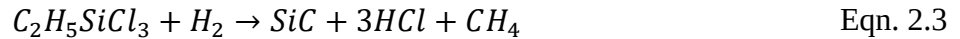
2.2.1 Crystal Structure of SiC

Pure SiC can be found in any of a few hundred polytypes, of which there are 4 major crystal structures, 3C, 4H, 6H, and 15R. The most common of these except at very high temperatures is the 3C variety which is the only cubic polytype, has three atomic layers to a unit cell and has the alternative name β -SiC. The next two in this list are hexagonal close packed structures with 4 (4H), and 6 (6H) atomic layers to a unit cell. The last, 15R, has a 15-atom repeating cell with rhombohedral structure. These and all other non-cubic polytypes are termed α -SiC [7, 21]. Due to the problematic nature of hexagonal structures under radiation, and the energetic stability considerations, 3C is the preferred variant for design, and the one formed most easily by the CVD method. A summary of the crystal structure of the SiC polytypes is given in Figure 2.2 and Table 2.2. The temperature-dependent lattice parameter of β -SiC, the crystal structure of interest for LWRs, is defined by the following equation from [21], with T in Kelvin and a in nm.

$$a = 0.43577 + 1.3887 \times 10^{-6}(T - 273) + 7.8494 \times 10^{-10}(T - 273)^2 - 2.4434 \times 10^{-13}(T - 273)^3 \quad \text{Eqn. 2.1}$$

2.2.2 Chemical Vapor Deposition (CVD)

CVD is the premier method for manufacturing of pure, high quality β -SiC [21, 22]. Unlike the methods in sections 2.2.3 and 2.2.4, CVD is a direct reaction that produces stoichiometric products, with very low impurity levels (see Table 2.3) at temperatures around 1200°C [21]. The synthesis process involves a chemical precursor which is carried by H₂, to a substrate, where it reacts in either of the following ways to form SiC with the theoretical density of 3.21 g/cm³ [22].



The most common precursor is methyltrichlorosilane (MTS), whose reaction to SiC is shown in Eqn. 2.2 [22, 23].

2.2.3 Sintering

Multiple sintering methods exist for SiC and every method is not discussed in depth here. Some additives and sintering aids used are B, C, Al₂O₃, Y₂O₃, CeO₂, ZrO₂, SiO₂, and TiC [15, 21, 24-30] to achieve good density. Because of the very large absorption cross-section of B [21, 31], and the excessive corrosion rate of Al₂O₃ (currently a necessary additive for adequate density) [14, 15, 27], obtaining good density without seriously compromising the viability SiC is a current topic of research. One of the most promising fabrication methods is NITE (nano-infiltration and transient eutectic phase) LPS (liquid phase sintering) [15]. Recently, some work has been done on spark plasma sintering (SPS) using high-energy ball milling, which produced

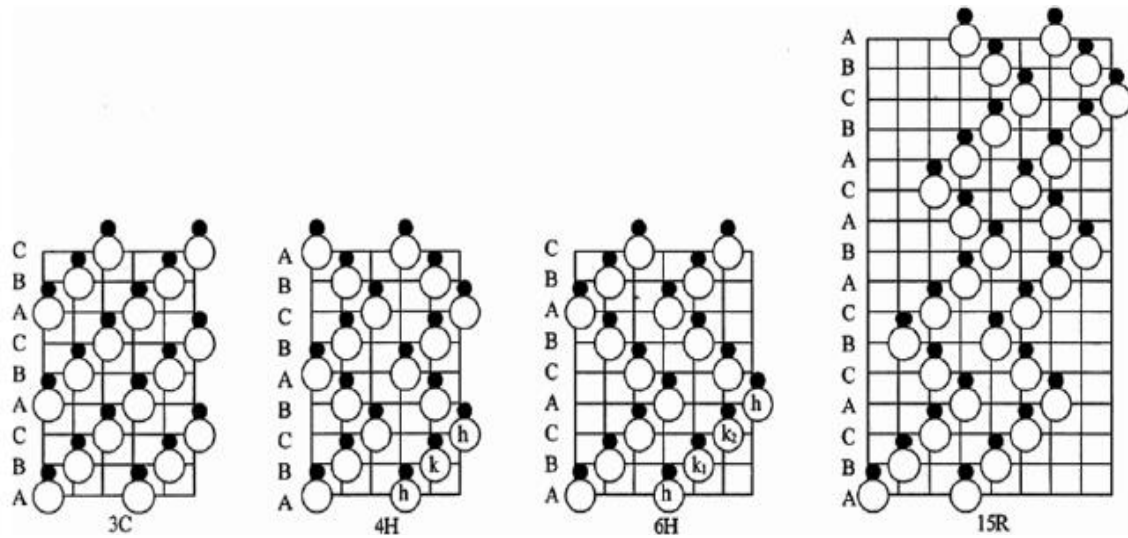


Figure 2.2: Depiction of the four major crystal structures of SiC. The number indicates the number of atoms along one side of the unit cell, while the letter designates the structure as either cubic (C), hexagonal (H), or Rhombohedral (R). The black and white circles represent C and Si, respectively. Reprinted from the Journal of Nuclear Materials 371, L.L. Snead, T. Nozawa, Y. Katoh, T.S. Byun, S. Kondo, D.A. Petti, Handbook of SiC properties for fuel performance modeling, 329-377, Copyright 2007, with permission from Elsevier [21].

Table 2.2: Crystal definitions of 5 major polytypes of SiC. Data from [21, 32]. Reprinted from the Journal of Nuclear Materials 371, L.L. Snead, T. Nozawa, Y. Katoh, T.S. Byun, S. Kondo, D.A. Petti, Handbook of SiC properties for fuel performance modeling, 329-377, Copyright 2007, with permission from Elsevier [21].

Polytype	Space Group	Element:	
		Wyckoff 1D, Position xyz	
2H	P63mc	Si: 2b, 1/3 2/3 0	C: 2b, 1/3 2/3 3/8
3C	F43m	Si: 4a, 0 0 0	C: 4c, 1/4 1/4 1/4
4H	P63mc	Si (1): 2a, 0 0 0	C (1): 2a, 0 0 3/16
		Si (2): 2b, 1/3 2/3 1/4	C (2): 2b, 1/3 2/3 7/16
6H	P63mc	Si (1): 2a, 0 0 0	C (1): 2a, 0 0 1/8
		Si (2): 2b, 0 0 1/2	C (2): 2b, 1/3 2/3 7/24
		Si (3): 2b, 1/3 2/3 5/6	C (3): 2b, 1/3 2/3 23/24
15R	R3m	Si (1): 3a, 0 0 0	C (1): 3a, 0 0 3/60
		Si (2): 3a, 0 0 2/15	C (2): 3a, 0 0 11/16
		Si (3): 3a, 0 0 6/15	C (3): 3a, 0 0 27/60
		Si (4): 3a, 0 0 9/15	C (4): 3a, 0 0 39/16
		Si (5): 3a, 0 0 13/15	C (5): 3a, 0 0 55/60

Table 2.3: Impurity levels in SiC materials available in 1996. Reprinted from the Journal of Nuclear Materials, 233-237 L.L. Snead, R.H. Jones, A. Kohyama, P. Fenici, Status of silicon carbide composites for fusion, 26-36, Copyright 1996, with permission from Elsevier [33].

<i>Element</i>	<i>CVD SiC (ppb)</i>	<i>Super SiCTM (ppb)</i>	<i>High NicalonTM (ppb)</i>	<i>SiC/SiC (ppb)</i>
<i>Fe</i>	<5	440	110,000	<4000
<i>Cr</i>	0.16	17	27,000	8000
<i>Co</i>	<0.67	13	770	120
<i>Ni</i>	205	74	12,000	4200
<i>Mo</i>	0.28	41	3900	-
<i>Zr</i>	<4.5	236	6100	<1800
<i>Ta</i>	<0.0057	-	120	-
<i>W</i>	0.688	32	1600	<110
<i>Pt</i>	-	542	62,000	<1000
<i>As</i>	5.7	3	2.8	-
<i>Na</i>	0.63	50	2200	320
<i>Al</i>	9.1	-	<20,000	<560

high density product with small grain boundaries and no additional sintering aids [34], an improvement over similarly processed SiC [35]. Additional studies are necessary to determine how SPS affects mechanical and chemical properties. Another form of sintering is hot pressing (HP), which uses the eutectic temperature of SiC and oxide sintering aids such as alumina and yttria [21].

2.2.4 Reaction Sintering (RS)

Also known as reaction-bonding (RB), this method uses a direct reaction between Si and C in a matrix of SiC particles at high temperatures ($\sim 1450^{\circ}\text{C}$). The Si is in either a vapor or liquid phase during this reaction, and some residual metallic Si is invariably incorporated into the matrix [21, 23, 36, 37]. This disrupts the integrity of the product, especially increasing susceptibility to corrosion. Moreover, it has been implicated in decreasing the elastic modulus of SiC [21].

2.2.5 Polymer infiltration and Pyrolysis (PIP)

PIP is a potentially valuable, low cost technique, which is of special interest in the manufacture of CMCs [23]. A preform (or mold) is filled under pressure with an appropriate polymer precursor. Subsequent heat treatment cross-links the polymers and then pyrolysis removes the polymer, leaving the SiC matrix behind. The main drawback to this technique is that it does not produce highly crystalline stoichiometric SiC, a significant detriment, especially with high temperature water [23].

2.2.6 Ceramic-Matrix Composites (CMCs)

CMCs of SiC are made by taking thin (~ 10 microns thick) fibers of various quality and composition (see Table 2.4) and weave them into a loose fabric preform. The fabric is then coated, by various means, with an interfacial layer, typically of pyrolytic carbon, followed by the matrix of SiC and possibly a CVD sealant coating [11, 22, 29, 38, 39]. The most robust coating method is chemical vapor infiltration (CVI) which produces a highly reproducible, high quality ceramic with good radiation-resistance properties [22, 33, 37]. In CVI, fibers are coated with nearly pure SiC by a process similar to CVD. However, because the precursors used must diffuse through the fiber preforms to make a dense matrix, CVI requires significantly longer times than CVD, and resulting CMCs are not theoretically dense (10-20% porosity) [22, 28, 38, 40]. As a result, these ceramics are very expensive (several thousand dollars for small laboratory samples) but represent the best quality of SiC technologies. The expense can be decreased by increasing deposition rates at the cost of increasing porosity, but this degrades the product substantially. An empirical model describing the CVI process is detailed in Deck et al. [22]. As a result of the sealing off of internal pores as the matrix builds, the density of the matrix is highest surrounding each fiber and on the outer edge of the sample, with any pores forming between fibers. Figure 2.3 demonstrates this effect, showing the size of the coating on fibers at different distances from the CMC surface partway through the process. That work also showed that an increasing temperature of deposition, helped to decrease pore formation.

Table 2.4: Properties of SiC-based fibers for CMCs of SiC available in 1996. Reprinted from the Journal of Nuclear Materials, 233-237 L.L. Snead, R.H. Jones, A. Kohyama, P. Fenici, Status of silicon carbide composites for fusion, 26-36, Copyright 1996, with permission from Elsevier [33]. Similar data is found in [41].

<i>Fiber</i>	<i>Composition and Structure</i>	σ_y (MPa)	E (GPa)	ρ (g/cm ³)	<i>Comment</i>
<i>Nicalon</i>	65% SiC, 23% SiO ₂ , 11% C (~3 nm β -SiC gains)	3	220	2.55	Available
<i>Hi-Nicalon</i>	77% SiC, 23% SiO ₂ , <0.5% O (10-100 nm β -SiC gains)	2.8	270	2.74	limited availability
<i>Nicalon-S</i>	95% SiC, 5% C (~3 nm β -SiC gains)	2.6	420	3.1	Limited availability
<i>Dow Corning SiC</i>	>99% SiC (30 nm β -SiC gains)	2.6	420	3.1	Limited availability
<i>Tyranno</i>	SiC, Ti-C-O (β -SiC grains)	2.5	190	2.35	Available
<i>HPZ</i>	Si, N, O, C (amorphous)	2.3	180	2.24	Available
<i>SCS-6</i>	CVD SiC on carbon	3.45	420	3.1	Unweavable

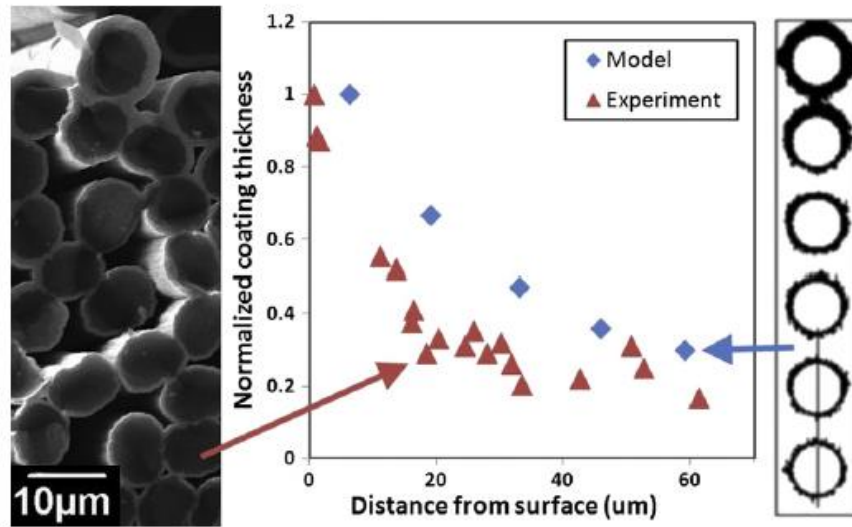


Figure 2.3: Effect of coating thickness on various fibers at different distances from the CMC surface part-way through the CVI process. Reprinted from Progress in Nuclear Technology, 57(Supplement C), C.P. Deck, H.E. Khalifa, B. Sammulu, T. Hilsabeck, C.A. Back, Fabrication of SiC–SiC composites for fuel cladding in advanced reactor designs, 38-45, Copyright 2012 with permission from Elsevier [22].

Other techniques are less expensive but produce lower quality products. These include polymer infiltration and pyrolysis (PIP), reaction sintering (RS), hot pressing (HP), nano-infiltration and transient eutectic sintering (NITE), and melt infiltration (MI) [21, 22, 26, 28, 29, 36, 38, 39, 42]. As with pure samples, RS produces CMCs with excess Si, an unacceptable impurity for LWR applications [37]. A shortcoming of HP and NITE is the presence of sintering aids required for good density corrode faster than SiC, leading accelerated attack of grain boundaries [14, 15, 37, 38]. Moreover, while a fully-dense matrix with high crystallinity is obtainable from the NITE process, NITE also requires high pressures, which can lead to damage of the fibers [38], however it performs satisfactorily under irradiation and gives the best density of available techniques [39, 40]. Current technological limitations make PIP and MI composites less fully crystalline; recent advances may soon solve this issue [37, 43]. An advantage of PIP is the possibility of more complex shapes. Possible combinations of these techniques may obtain both suitable materials properties while decreasing the overall cost, as with the slip infiltration-based (SITE) ceramic [44].

In addition to matrix fabrication methods, the choice of fibers in CMCs is critical to the integrity of the product. Several authors [5, 23, 26, 28, 33, 39-41, 43, 45-47] have discussed the substantial problems of first-generation NicalonTM fibers, and the benefits of using generation III fibers such as Tyranno-SA3, or Hi NicalonTM Type S (Nicalon-S). Fiber quality is defined by the degree of pure SiC which is achieved, as well as minimization of pure carbon used in fiber-matrix interfaces, and elimination of oxygen [23, 40]. NicalonTM fibers themselves do not perform well under irradiation [33, 48]. Across these multiple manufacturing types, materials properties tend to remain uncompromised, although better strength [37]. Materials properties for a variety of available fibers are shown in Table 2.4 from Snead et al., [49]. More detailed properties for CMCs with high quality fibers and CVD SiC are given in [20].

The fiber-matrix interface is another vital component of CMCs. It is responsible for crack arrest and transfer of stress from the brittle matrix to the fibers [20, 22, 23, 26, 29, 33, 39-41, 44, 50]. Stone et al., [20], showed that this behavior is essential use of SiC in LWRs since micro-cracks form following a single 18 month reactor cycle. Without the fiber-matrix interfaces, these cracks would cause catastrophic failure of the cladding, as illustrated in Figure 2.4 by showing the stress-strain curve of SiC CMCs with NicalonTM fibers constructed with interface thicknesses up to 1 micron. Failure of CMCs with no interface (uncoated) were reported to fail at ~50 MPa, compared to 250 MPa for just 100 nm of PyC.

Common interfaces consist of PyC (pyrolytic carbon), boron nitride, multilayer PyC/SiC or BN/SiC [23, 26, 28, 29, 38-40, 47]. For LWR applications, BN provides an unacceptable neutronic penalty, so it is not considered further here. PyC interfaces are generally optimized between 50 and 200 nm generating good mechanical properties, and improved radiation resistance in multilayer form, but may have reduced debonding shear stress under irradiation than a single layer form [40, 47].

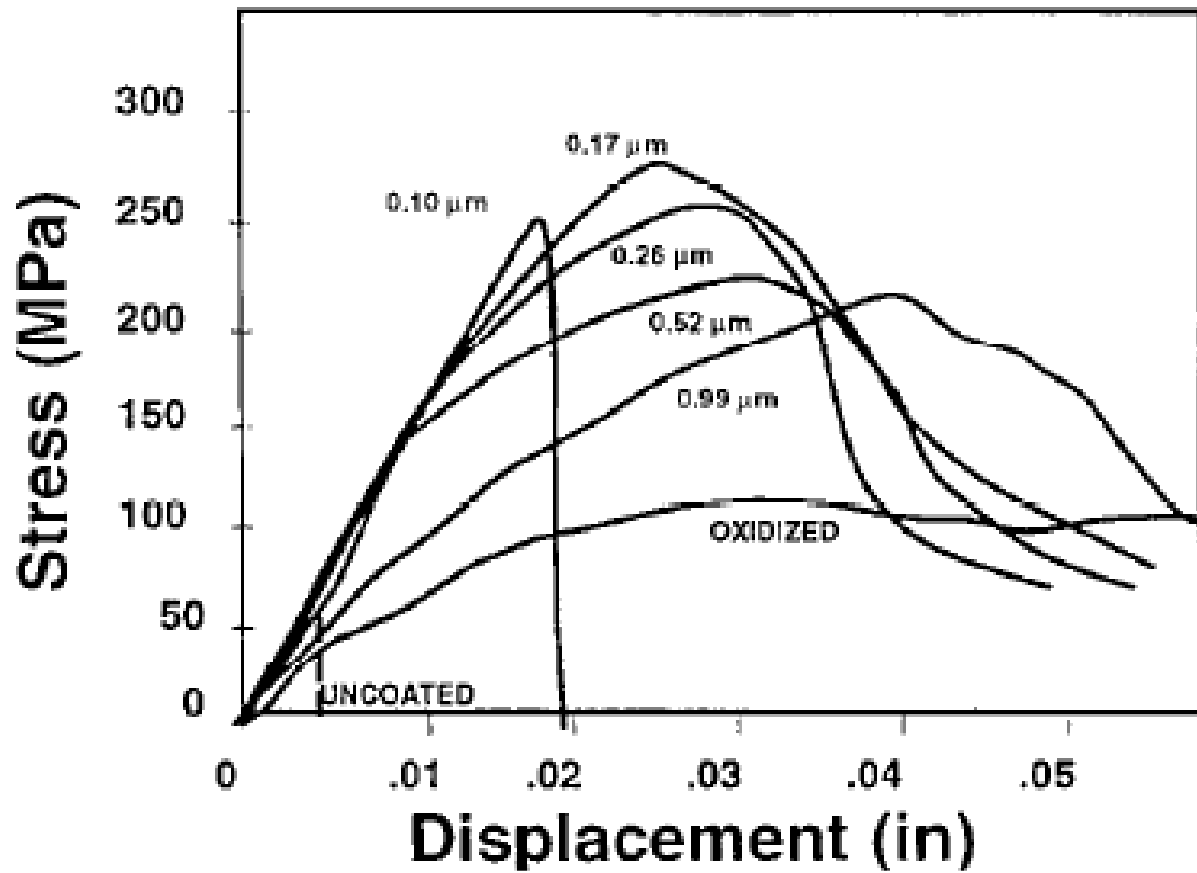


Figure 2.4: stress-strain curve of SiC CMC composed of NicalonTM fibers with a carbon interface of various thicknesses up to 1 micron. Reprinted from the Journal of Nuclear Materials, 233-237 L.L. Snead, R.H. Jones, A. Kohyama, P. Fenici, Status of silicon carbide composites for fusion, 26-36, Copyright 1996, with permission from Elsevier [33].

Unfortunately, it is also highly susceptible to oxidation removal, thereby accelerating the corrosion mass loss in LWRs if the CVD overcoat is penetrated [23, 51, 52].

Figure 2.4 demonstrates the effect of interface thickness on tensile stress of the CMC. In Nicalon-S-based CMCs, interfacial stresses for simple PyC (pyrolytic carbon) interfaces do not decrease with irradiation, whereas multi-layered (ML) interfaces showed decreased frictional stress as measured by push-out tests [40]. Additional concerns regarding interface degradation of PyC has led to some interest in MAX-phase interfaces, due to better irradiation performance with excellent mechanical and thermal properties [23, 53]. Fabrication challenges remain to be solved before this material can be tested as an interface.

2.3 Mechanical Properties

Pure CVD SiC has good mechanical properties for LWR conditions, and the highest elastic modulus of the various SiC fabrication methods [21, 23, 40]. In order for these properties to be consistent and to decrease fracture probabilities, CMCs are necessary, which requires compromise in other properties like thermal conductivity (section 2.4). With CMC SiC, which has an appropriate interface, cracks can be arrested through a decreased interfacial bond strength [33, 40]. Initially exhibiting linear-elastic tensile behavior, micro-crack formation in the matrix causes the deformation mode to become non-linear [20]. In either CMC or pure SiC, grain size has no observed effect on elastic modulus, while the pore size/volume, and impurity concentrations decrease the modulus through introduction of stress concentrators [21, 22]. Fabrication of CMCs, using sintering additives, or producing less dense SiC degrades the elastic modulus, but the grain size and crystal structure do not appear to affect the modulus [21, 26, 38]. Porosity decreases the modulus as shown below in Figure 2.5 for pure SiC and Figure 2.6 for CMC SiC with Tyranno fibers formed by CVI [38, 40]. The Poisson's ratio has been observed in a range of 0.13-0.21, with lower values being obtained for more impure and/or porous SiC and $\nu = 0.21$ for CVD SiC, with no significant temperature dependence [21].

The hardness of SiC is high enough that it is widely used as an abrasive in grinding and polishing media. However, specific values of hardness depend strongly on the porosity, impurities, and fabrication process since hardness is fundamentally measuring bond strength, crack initiation and propagation resistance, and internal defect sizes [21, 35]. Hardness has been extensively measured for alpha and beta SiC for various fabrication methods and sintering additives. Some compiled data is presented by Snead et al. [21] and is reproduced below in Table 2.5.

Compiled fracture toughness values are presented by Snead et al. [21] for a variety of manufacturing methods, sintering additives, and methods of measurement. Because of the partially ionic nature of the Si-C bond, it is subject to fast crack propagation, requiring the use of CMCs. Therefore, the impurities introduced from sintering, as well as the pore and defect structure differences between manufacturing methods cause no statistically significant difference in fracture toughness, which has been reported as $\sim 2.5\text{-}4.5 \text{ MPa m}^{0.5}$ corresponding to fracture energies of $\sim 15\text{-}30 \text{ J/m}^2$. Per Hasegawa et al [41], this is about an order of magnitude lower than typical CMC SiC materials.

Table 2.5: Hardness of various SiC materials at room temperature. Reprinted from the Journal of Nuclear Materials 371, L.L. Snead, T. Nozawa, Y. Katoh, T.S. Byun, S. Kondo, D.A. Petti, Handbook of SiC properties for fuel performance modeling, 329-377, Copyright 2007, with permission from Elsevier [21].

Material	Sintering additives	Vickers Hardness (GPa)	Knoop Hardness (GPa)
Sintered α -SiC	B, C	24.9-26.7	22.4-27.4
Hot-pressed α -SiC	Al ₂ O ₃ , WC, Co	19.3	22.3
Hot isostatic pressed α -SiC	AlN	25.0-27.3	n/a
CVD β -SiC	-	20.7-24.5	24.5
Sintered β -SiC	B, C	21.1-23.9	20.9
Hot-pressed β -SiC	Al	26.7-29.7	n/a
Hot-pressed β -SiC	Al ₂ O ₃ , RE ₂ O ₃ (RE = La, Nd, Y, Yb)	3.4-21.2	n/a

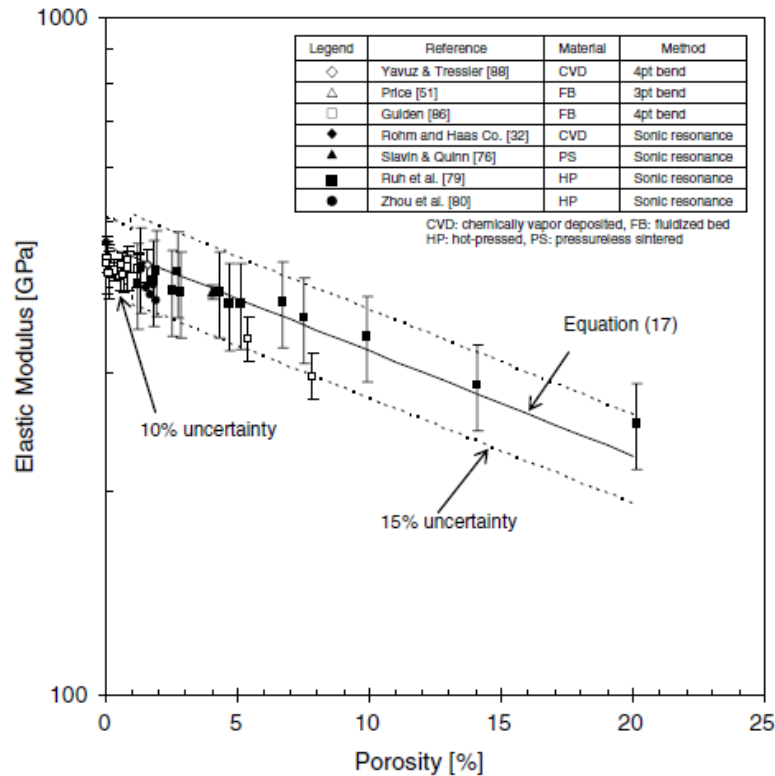


Figure 2.5: Effect of porosity on the elastic modulus of pure SiC for a variety of manufacturing methods. Reprinted from the Journal of Nuclear Materials 371, L.L. Snead, T. Nozawa, Y. Katoh, T.S. Byun, S. Kondo, D.A. Petti, Handbook of SiC properties for fuel performance modeling, 329-377, Copyright 2007, with permission from Elsevier [21].

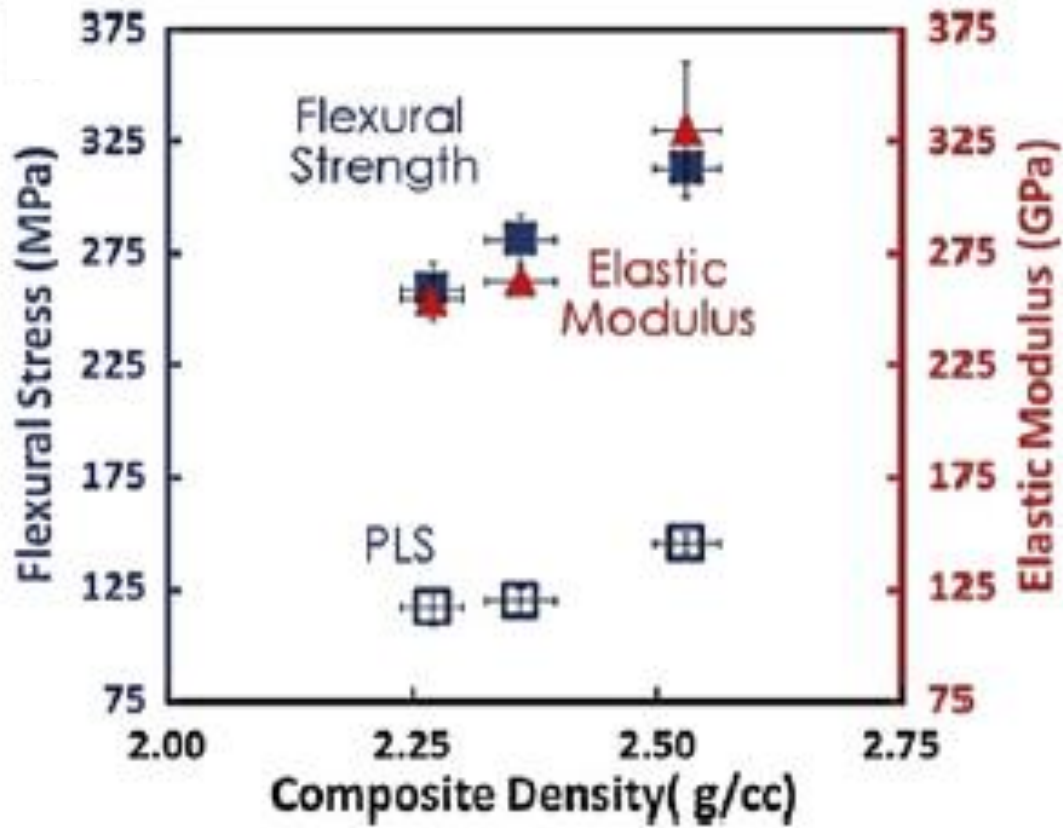


Figure 2.6: Variation of flexural strength and elastic modulus with CMC density where composites were formed by the CVI process using Tyranno fibers. Reprinted from Progress in Nuclear Technology, 57(Supplement C), C.P. Deck, H.E. Khalifa, B. Sammulu, T. Hilsabeck, C.A. Back, Fabrication of SiC–SiC composites for fuel cladding in advanced reactor designs, 38-45, Copyright 2012 with permission from Elsevier [22].

The Weibull modulus, m , and characteristic strength, σ_0 , have similarly been tabulated for β -SiC [21]. The value of the modulus is highly dependent on the test type and specimen geometry. For tensile testing, $m = 7-11$, while ring compression yields $m = 3-9$. As appropriate for engineering applications, bulk β -SiC characteristic strengths range between 200 and 460 MPa. Strength dependence on temperature is further strongly dependent on temperature. CVD SiC is nearly constant up to ~ 1400 K, and increases up to ~ 1800 K before any degradation is observed [21]. The defects that other manufacturing methods introduce become especially significant at higher temperatures, leading to degradation in strength with temperature, as shown in Figure 2.7. For CMC's, the Weibull modulus is similar, with a significantly higher characteristic strength (700-900 MPa) [40, 54]. Figure 2.8 compares the strength of CMC SiC to various materials.

For pure CVD SiC, thermal creep is induced in HCP crystals near 800°C by slip on basal plane, whereas steady-state creep is not observed in cubic crystals until above 1400°C by slip on close-packed planes [21, 40, 55]. Below this threshold only primary creep can be adequately measured [21]. Both of these are well outside of the range of interest for LWRs. Impure SiC from RS, HP, NITE, etc. materials have been observed to creep at accelerated rates due to the segregation to grain boundaries of intrinsic defects from these processes [21]. For CVD SiC with less than 500 ppm of impurities, the maximum creep rate is empirically described by,

$$\dot{\epsilon}_c = A_s \left(\frac{\sigma}{G}\right)^n \exp\left(-\frac{Q}{k_b T}\right) = 2000 \left(\frac{\sigma}{G}\right)^{2.3} \exp\left(-\frac{174 \frac{\text{kJ}}{\text{mol}}}{k_b T}\right) \quad \text{Eqn. 2.4}$$

where, G is the shear modulus, σ is the normal stress, Q is the activation energy, k_b is Boltzmann's constant, and T is the temperature (K). Using these values, the steady state creep rate for beyond the worst condition expected for a SiC fuel rod under PWR conditions (see Table 2.1: 20 MPa stress, $E = 460$ GPa [21], $T = 600$ K, $t = 54$ months), is $\sim 10^{-21} \text{ s}^{-1}$ for a total creep of $\sim 1.5 \times 10^{-13}$; steady-state creep is irrelevant for LWR fuel rod applications.

Thermal expansion of β -SiC is important for ensuring that the fuel pins have the appropriate volume at temperature. Fitting experimental data to the expected equation, high quality CVD SiC between 125 and 550 K has a coefficient of thermal expansion (CTE) of,

$$\alpha = 2.08 + 4.51 \times 10^{-3} T - 1.68 \times 10^{-6} T^2 \quad \left[\frac{10^{-6}}{\text{K}} \right] \quad \text{Eqn. 2.5}$$

In the temperature range of 550-1273 K, the CTE is best described by,

$$\alpha = -1.8276 + 0.0178 T - 1.5544 \times 10^{-5} T^2 + 4.5246 \times 10^{-9} T^3 \quad \left[\frac{10^{-6}}{\text{K}} \right] \quad \text{Eqn. 2.6}$$

within 10% of the true value.

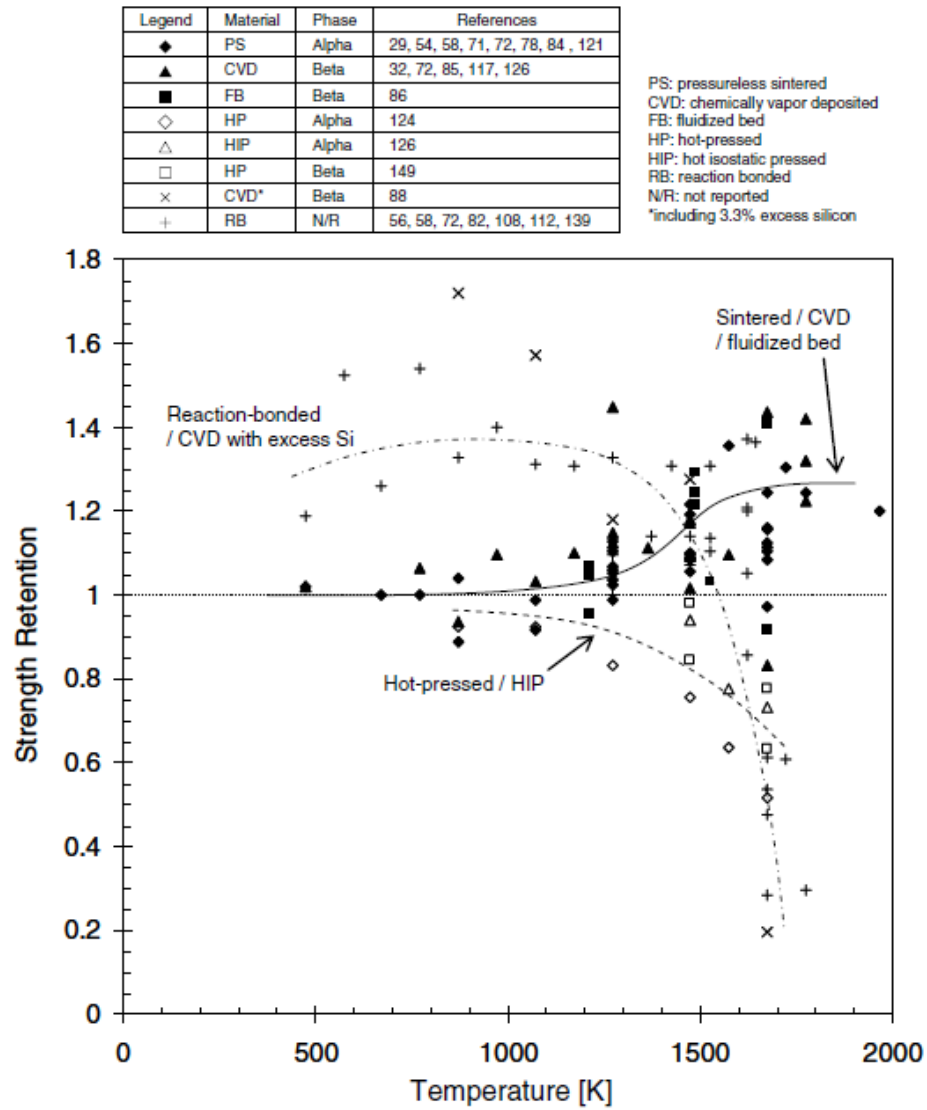


Figure 2.7: Relative tensile, flexural, and ring compression strength of SiC with different manufacturing methods. Reprinted from the Journal of Nuclear Materials 371, L.L. Snead, T. Nozawa, Y. Katoh, T.S. Byun, S. Kondo, D.A. Petti, Handbook of SiC properties for fuel performance modeling, 329-377, Copyright 2007, with permission from Elsevier [21]

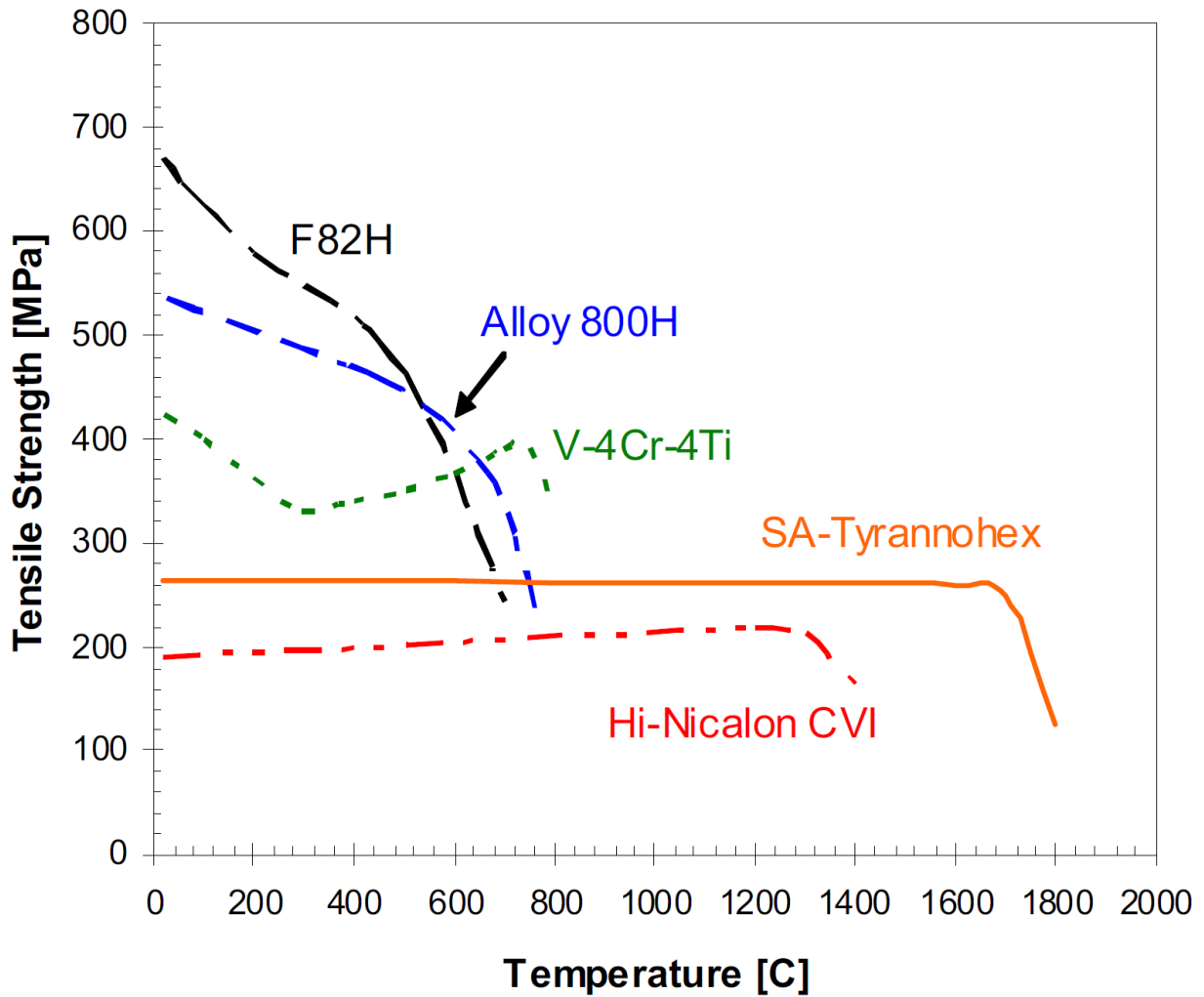


Figure 2.8: Comparison of SiC CMC strength to various materials. Reprinted from Fusion Science and Technology, 56, Y. Katoh, L.L. Snead, Operating Temperature Window for SiC Ceramics and Composites for Fusion Energy Applications, 1045-1052, Copyright 2009, with permission from Elsevier. Similar data is found in [40].

Above 1273K, CVD SiC has a CTE of about $5.0 \times 10^{-6}/\text{K}$ [21]. These equations are very close to the prediction using the lattice parameter relationship given in Eqn. 2.1.

2.4 Thermal Conductivity

The thermal conductivity of SiC has also been extensively studied [7, 21, 22, 33, 40, 50, 55]. Because SiC is not an electrical conductor, its thermal conductivity is directly dependent on phonon transport and thus the number of phonon scattering sites in a material, the fabrication method, porosity, grain boundaries, and impurity content (including sintering additives) all affect the thermal conductivity. Figure 2.9 demonstrates this; the thermal conductivity is significantly higher and follows the appropriate temperature dependence for high quality CVD SiC, and decreases substantially as additional phonon scattering sites (e.g. fiber-matrix interfaces) are added [50, 56]. The same is shown in Figure 2.11 which demonstrates that decreasing grain size will decrease conductivity at any given temperature. In CMCs, there is an additional effect of fiber orientation on thermal conductivity (see Figure 2.10). Similar data has been published from other authors [22, 40, 46, 56].

2.5 Crack Propagation Mechanisms in CMCs

CMCs provide excellent crack tolerance as a result of debonding on the fiber-matrix interface [21, 50, 56]. Crack propagation occurs by one of several mechanisms, which depend on strain, temperature, oxygen concentration, and load time primarily. Embrittlement by oxidation occurs in environments where SiO_2 can form on the fibers, below a critical temperature (see section 2.9.1). Removal of the interface by oxidation occurs when some oxygen is present, while relaxation of the fiber with irradiation creep is enhanced with low levels of oxygen. As temperatures increase, the stress rupture of the fibers becomes prominent [56]. The specific temperature and oxygen regimes in which these mechanisms occur are shown below and depend strongly on the time of exposure.

2.6 Hermeticity

While also applicable for fusion applications [7, 37], a good hermetic seal is essential to the qualification of a fuel rod, as significant fission gas release poses radiation contamination concerns in the entire plant process (for BWRs) or the primary coolant loop (PWRs). In fusion systems, coatings will be needed on CMCs because of the need to contain He coolants [37]. Since the fission gases which need to be contained are significantly larger (Rn , etc.), these seals may not be needed for fuel rod applications in LWRs. Some recent work suggests special precautions are unnecessary for a good seal [19].

2.7 Joining of SiC

Even if pre-made SiC specimens have the necessary properties at the desired conditions, it is essential that they be able to be joined together and with metal components, especially when SiC_t/SiC composites will be used for structural applications rather than the fuel cladding applications being investigated here.

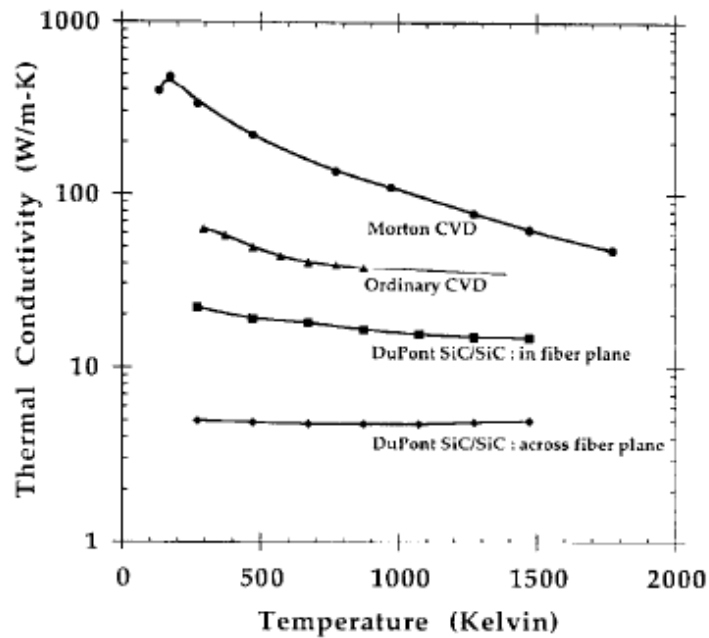


Figure 2.9: Thermal conductivity dependence of CVD SiC on temperature as a function of fabrication type. Reprinted from the Journal of Nuclear Materials, 233-237 L.L. Snead, R.H. Jones, A. Kohyama, P. Fenici, Status of silicon carbide composites for fusion, 26-36, Copyright 1996, with permission from Elsevier [33].

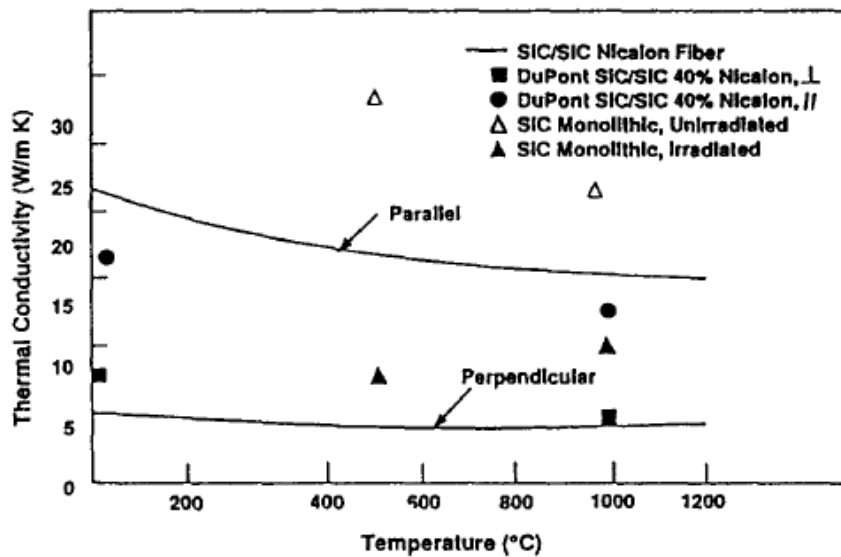


Figure 2.10: Thermal conductivity comparison of CVD and CMC SiC with different fiber orientations. Reprinted from the Journal of Nuclear Materials, 219, R.H. Jones, C.H. Henager, Jr., Fusion reactor application issues for low activation SiC/SiC composites, 55-62, Copyright 1995, with permission from Elsevier [50].

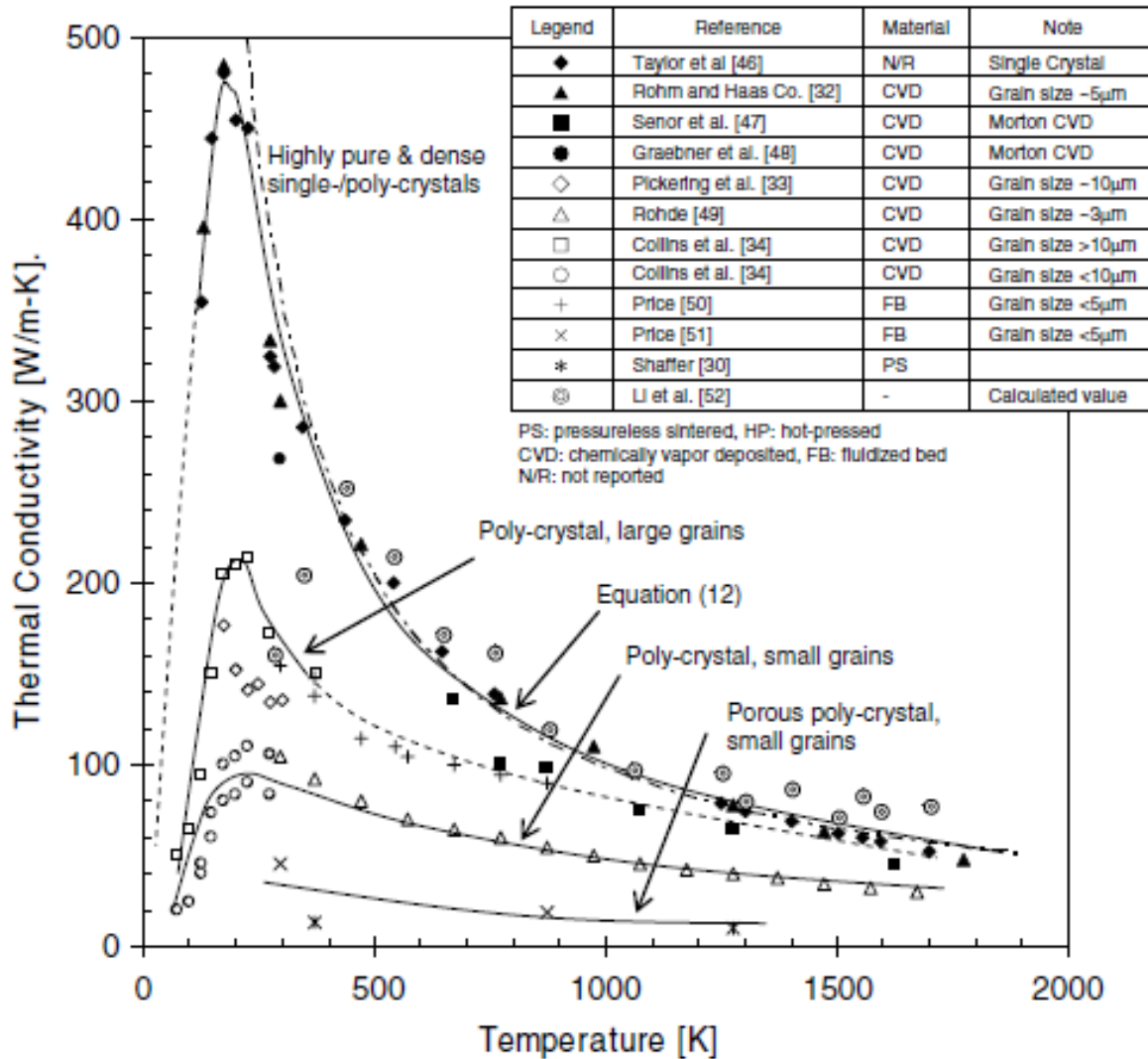


Figure 2.11: Thermal conductivity of SiC as evaluated by multiple studies. Reprinted from the Journal of Nuclear Materials 371, L.L. Snead, T. Nozawa, Y. Katoh, T.S. Byun, S. Kondo, D.A. Petti, Handbook of SiC properties for fuel performance modeling, 329-377, Copyright 2007, with permission from Elsevier [21]. Decreased grain size substantially reducing conductivity.

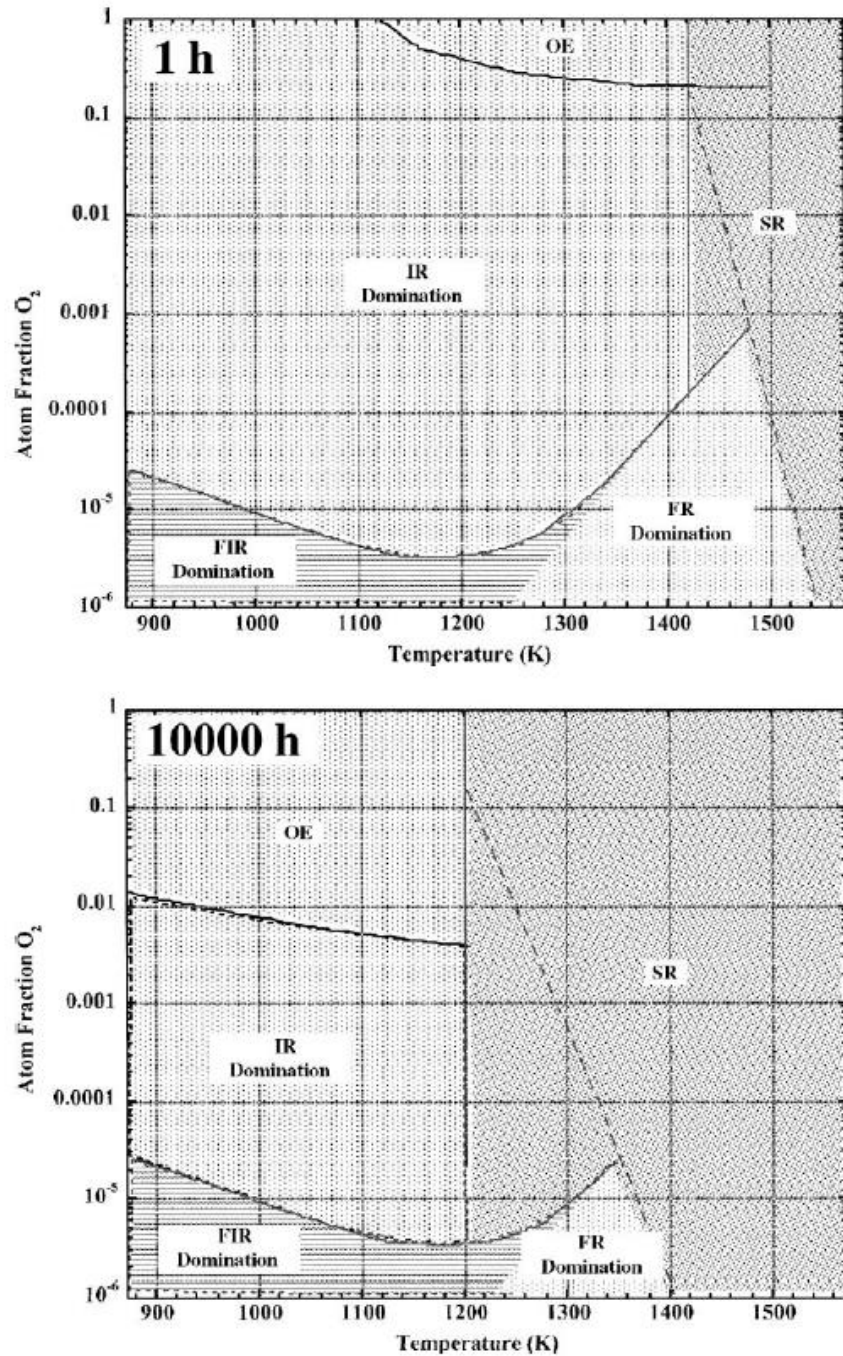


Figure 2.12: Variation of crack growth mechanisms with temperature and time for SiC/SiC composites using a PyC interface. OE is oxygen embrittlement, IR is interface replacement, SR is stress rupture, FR is fiber relaxation, and FIR is fiber irradiation creep. Reprinted from the Journal of Nuclear Materials, 307-311, R.H. Jones, L. Giancarli, A. Hasegawa, Y. Katoh, A. Kohyama, B. Riccardi, L.L. Snead, W.J. Weber, Promise and challenges of SiCf/SiC composites for fusion energy applications, 1057-1072, Copyright 2002, with permission from Elsevier [56].

While much effort has been devoted to this topic, joining technologies are still unable to perform adequately for nuclear reactor conditions [23, 37, 42, 57-59]. Some methods that show promise use the SiC chemical polymer precursor, polyhydromethylsiloxane (PHMS), as a joining filler, as well as NITE LPS SiC/SiC [58]. The latter of these yields high-strength joints but is not easily applicable for field-use because of the high pressures and temperatures needed for a good yield. Many other methods have been developed which may be successful for non-aqueous conditions, but which are not viable for LWRs due to corrosion-susceptibility or high neutron cross-sections of components such as B, Al₂O₃, etc. [44, 50, 58, 60]. Another significant issue is the presence of cracks through the joining medium [44]. As with interfaces, MAX-phase ceramics show some promise as a joining material for SiC, if it can be manufactured properly [23]. Some work has been done recently on the corrosion of joints formed by Ti-Si-C RS, SiC nanopowder sintering, and Mo and Ti interlayers. This work showed that all but the Mo joining technique survived hydrothermal corrosion up to five weeks [61]. Additional studies have presented joints with potentially acceptable mechanical properties, but these still must be fully qualified for hydrothermal corrosion and field applicability [60]. A good review of prospective joining methods is found in [58].

2.8 Radiation Effects

Radiation effects in SiC have been characterized extensively [21, 37, 40, 56]. In general, effects are divided into three temperature regimes: amorphization (<150°C), swelling saturation (150-800°C), and void swelling (>1000°C) with a transition region between 800 and 1000°C [7, 21, 44, 55]. SiC is considered to be radiation-resistant up to high temperatures, especially in the β phase, as shown in the following sub-sections [1, 7, 21, 37, 40, 55, 56, 62, 63]. However, impurities can cause substantial degradation in the radiation tolerance [7, 21, 64]. SiC fibers behave similarly to cubic SiC when the fiber is highly crystalline and near-stoichiometric composition [40].

2.8.1 Amorphization

Amorphization of SiC is a low temperature phenomenon (<423 K) [21, 33, 56] and is preceded by excessive swelling which induces significant matrix strain logarithmically with dose [21]. Upon amorphization, the hardness and elastic modulus of SiC drastically change along with about a 10-15% increase in volume. Under ion irradiation the threshold amorphization temperature and threshold dose depends significantly on the exact irradiation conditions, Figure 2.13. Since there is no reason to suspect that amorphization will occur for LWR-relevant conditions, the topic is not further commented on here [65].

2.8.2 Defect Microstructure Evolution

For high quality CVD SiC, below about 800°C, radiation-induced defects in β -SiC are predominately black spots and small dislocation loops [21, 37]. This microstructure saturates at about 0.5-2 dpa in the recombination dominant regime [21, 49]. At low temperatures large Frank loops may also form when damage becomes high [21]. As temperatures increase, the mobility of these defects increases, allowing formation of larger loops and dislocations up to a temperature

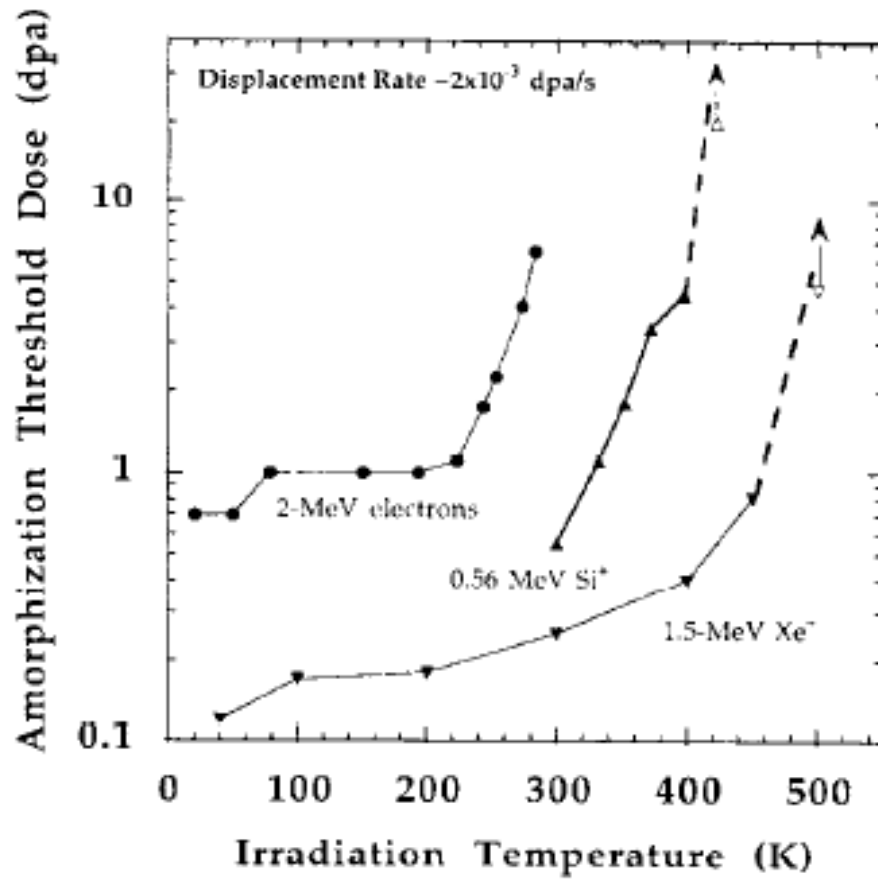
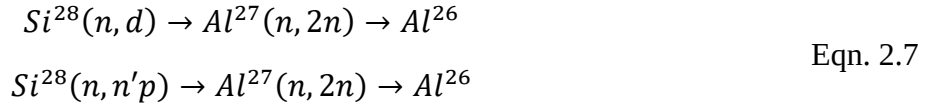


Figure 2.13: Threshold dose for amorphization of SiC as a function of irradiation temperature. Three different ions were used with energies such that the displacement rate was 2×10^{-3} dpa/s. Reprinted from the Journal of Nuclear Materials, 233-237 L.L. Snead, R.H. Jones, A. Kohyama, P. Fenici, Status of silicon carbide composites for fusion, 26-36, Copyright 1996, with permission from Elsevier [33].

of 1400°C Moreover, black spots become coarse [21] and cavities have also been observed with self-ion irradiation [37]. Si vacancies become mobile around 800-900°C, and void swelling becomes possible via 3D cluster formation [21]. These vacancies tend to then migrate to sinks, specifically stacking faults, where voids form preferentially.

2.8.3 Neutron Activation and Transmutation

Neutron activation of SiC is insignificant under LWR conditions, because the reactions have multi-MeV thresholds and very low cross-sections below 14 MeV [5, 33, 66]. These reactions are presented below.



Of greater significance, nuclear transmutation can produce a substantial quantity of H and He in SiC for fusion applications [37]. Ion irradiations have shown that the presence of He can significantly reduce the temperatures at which stable voids can form, and can stabilize Frank loops and dislocation networks [37].

2.8.4 Volumetric Swelling

Below about 1200°C and above the amorphization threshold (where interstitials become mobile) point defect swelling dominates due to negligible vacancy migration. As temperatures increase, point defect-induced swelling decreases through enhanced recombination of interstitials prior to their absorption in clusters [21, 23, 40]. Above 1200°C for neutron irradiation, and 1000°C for ion irradiation [21], swelling is caused by tetrahedral voids which monotonically swell with dose, as a consequence of the Si vacancies becoming mobile. This is the void swelling regime where cavities dominate the volumetric change. CMC SiC infiltrated by CVI swells like monolithic β -SiC. This behavior has been commonly observed as shown in Figure 2.14. For certain Gen IV and fusion applications, which may use temperatures above 1000°C, swelling increases with temperature and does not appear to saturate with dose above 1200°C indicating significant diffusion rates of vacancies and correspondingly high binding energies of vacancies in clusters that prevent dissolution at high temperature [21, 37, 55]. A more complete swelling profile is given in Figure 2.15. Impurities in the SiC also can dramatically increase observed swelling [67, 68]. While this study used the step height method to determine swelling (from ion irradiation), the work qualitatively shows an increase in swelling with impurities.

Below 1000°C the swelling mechanism is not dominated by aggregated vacancies, but rather by individual or very small vacancy clusters along with other point or dislocation loop-type defects. This means that at LWR-relevant temperatures, near 300°C, swelling saturates at only ~1-2%, by 0.1 to ~2 dpa. Therefore, SiC components can be appropriately designed for long-term use as long as the crystal structure is cubic (i.e., only β -SiC should be used) [7, 20, 21, 23, 69]. Moreover, the actual values of swelling are strongly dependent on temperature with 200°C irradiations yielding highest swelling (2%), with significant reduction as temperatures increase [21, 37].

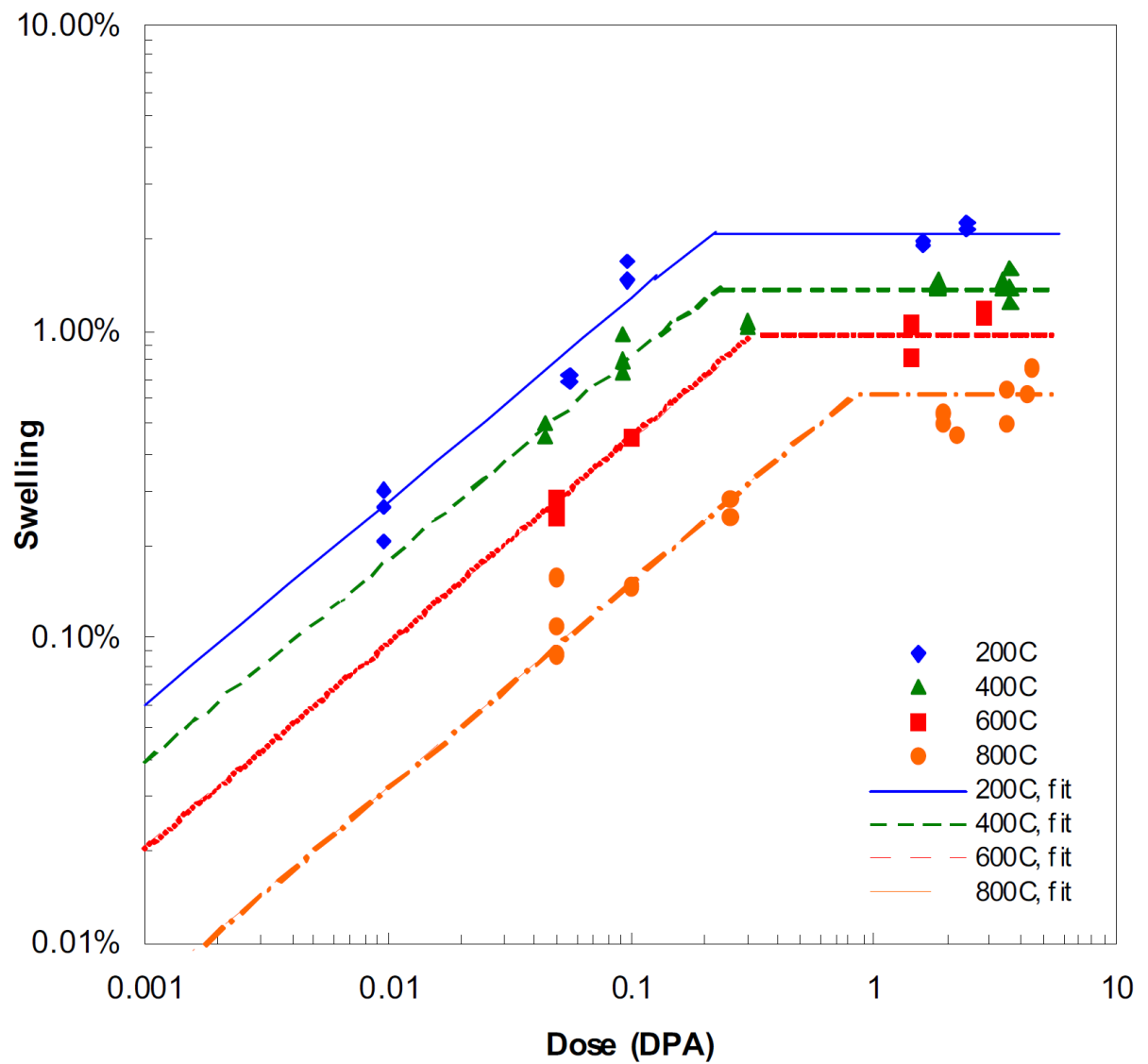


Figure 2.14: Swelling of SiC as a function of temperature and damage. Reprinted from Fusion Science and Technology, 56, Y. Katoh, L.L. Snead, Operating Temperature Window for SiC Ceramics and Composites for Fusion Energy Applications, 1045-1052, Copyright 2009, with permission from Elsevier [55] .

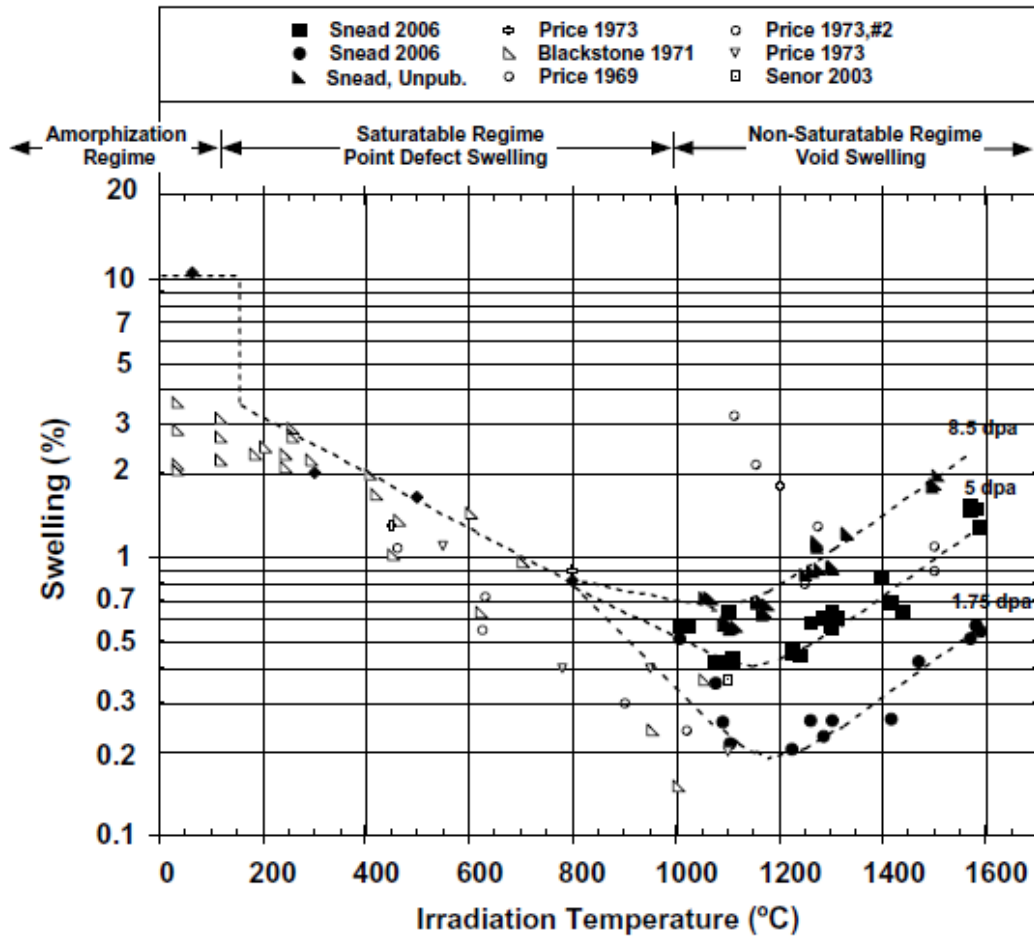


Figure 2.15: Swelling of SiC across all radiation damage regimes. Reprinted from the Journal of Nuclear Materials 371, L.L. Snead, T. Nozawa, Y. Katoh, T.S. Byun, S. Kondo, D.A. Petti, Handbook of SiC properties for fuel performance modeling, 329-377, Copyright 2007, with permission from Elsevier [21]. Similar plots are found in [40, 41, 68]

2.8.5 Coefficient of thermal expansion

The CTE of SiC has also been well characterized both with and without irradiation. For CMCs with highly crystalline, near-stoichiometric fibers, irradiation at temperatures of interest to ~6 dpa shows no degradation of the CTE relative to unirradiated CVD SiC [40]. This is shown in Figure 2.16.

2.8.6 Mechanical Property degradation

PIP fibers decrease in size due to neutron irradiation if they are not fully crystallized [69], decreasing fracture strength and elastic modulus. When properly crystallized, flexural strength is not observed to degrade by irradiation up to at least 12 and 20 dpa for CMC CVI, and CVD SiC, respectively [21, 37, 55]. Some recent research suggests that NITE-fabricated SiC irradiated up to $\sim 5 \times 10^{24}$ n/m² showed no strength degradations between 750 and 1000°C. Figure 2.17 demonstrates how fiber quality effects this degradation, indicating the need for use of advanced fibers such as Nicalon-S or Tyranno-SA3. Similar results are shown in [40, 49, 56]. The wide differences in strength dependence on irradiation is due to grain boundary composition [21]. Every sintering method of necessity introduces impurities into the matrix which segregate to grain boundaries, increasing failure probabilities. Specific additives will also react with neutrons. Boron, for example, undergoes an (n, α) reaction, further degrading the material through He bubble formation [21]. Other non-CVD formation methods suffer from strength degradation. The excess Si in RS (RB) SiC, also segregates at grain boundaries causing strength reduction under irradiation. Figure 2.18 shows this degradation with increasing dose.

The elastic modulus of high purity CVD SiC degrades with increased swelling in the point defect swelling regime, but returns to the pre-irradiated values at high temperatures, as shown by Figure 2.19 [21, 23]. In the point defect swelling regime, the numerous point defects cause the matrix to relax as it expands. This has been shown to correlate such that 1% swelling results in 10% reduction in the elastic modulus [21]. In the void swelling regime, the matrix is swelled by accumulation of voids and point defect concentrations are reduced by the extensive sinks. This leads to a restoration of the original lattice parameter, and the corresponding original elastic modulus [21]. In contrast, hardness measurements show no dependence on temperature and are nearly identical to the un-irradiated hardness values, while there is some indication that fracture toughness may increase with irradiation in the point defect swelling regime [21]. The Weibull statistics mentioned in section 2.3 have been observed to change with increasing dose, indicating greater scatter in reported flexural strength data obtained by a four point bend test [21]. Moreover, the strength increased with temperature from 450 to 592 MPa over the range of 300-800°C, and $m = 6.2 - 8.7$ over the same range (from 9.2 unirradiated). These values are highly variable and may not be significant, but are likely to increase with well-controlled fabrication [21, 40]. In contrast, no change in ultimate strength or modulus was observed for CMC samples [40, 54]. More valuable data has been generated by tubular internal pressurization at different irradiation levels. This is presented below in Figure 2.20 and shows an increase of about 40 MPa at 2 dpa irradiated at 1000°C with a drop to 3.9 from 6.9 in the Weibull modulus. These

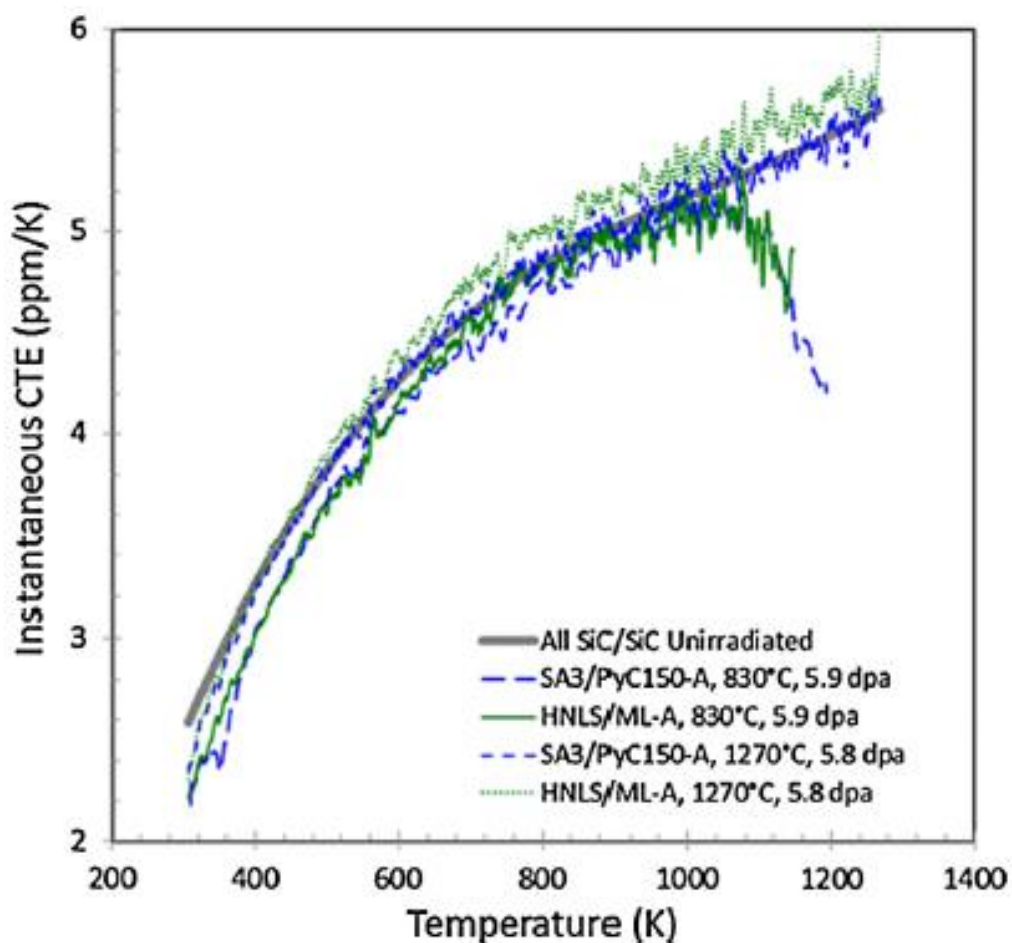


Figure 2.16: The variation of the CTE with temperature and irradiation damage. Reprinted from the Journal of Nuclear Materials, 448, Y. Katoh, K. Ozawa, C. Shih, T. Nozawa, R.J. Shinavski, A. Hasegawa, L.L. Snead, Continuous SiC fiber, CVI SiC matrix composites for nuclear applications: Properties and irradiation effects, 448-476, Copyright 2014, with permission from Elsevier [40].

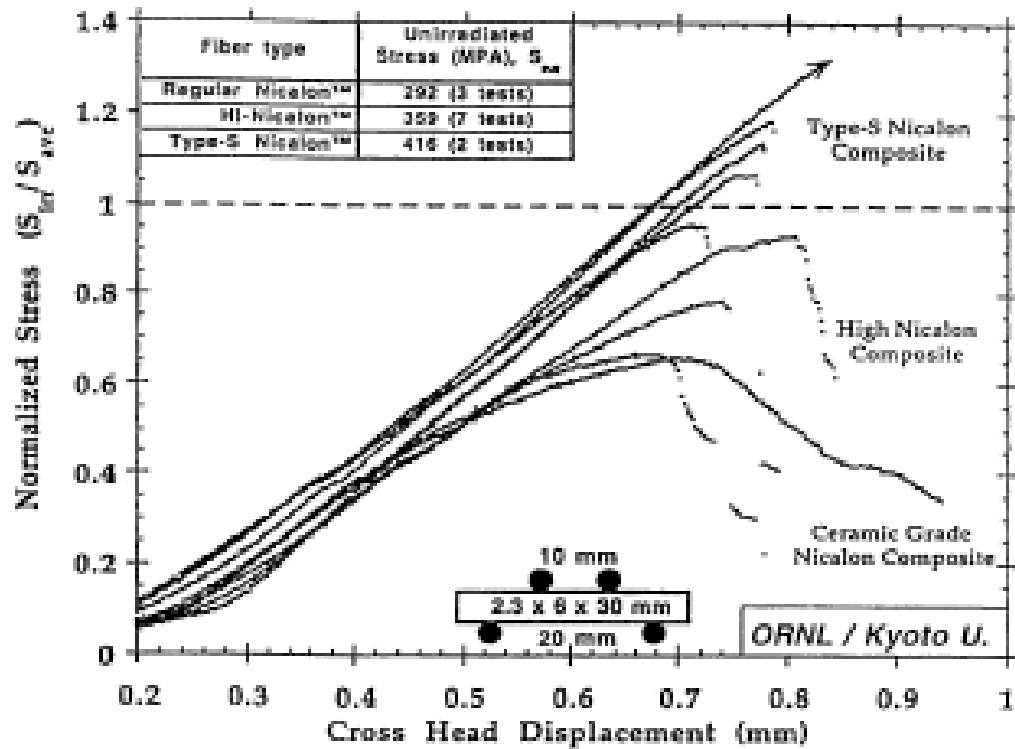


Figure 2.17: Comparison of strength degradation of various SiC_f/SiC CMCs at 1 dpa. Higher grades of Nicalon™ fibers degrade substantially less, or increase in strength relative to the original fiber. Reprinted from Fusion Engineering and Design, 55, A.R. Raffray, R. Jones, G. Aiello, M. Billone, L. Giancarli, H. Golfier, H. A., Y. Katoh, K. A., S. Nishio, B. Riccardi, M.S. Tillack, Design and material issues for high performance SiC_f/SiC-based fusion power cores, 55-95, Copyright 2001, with permission from Elsevier [69].

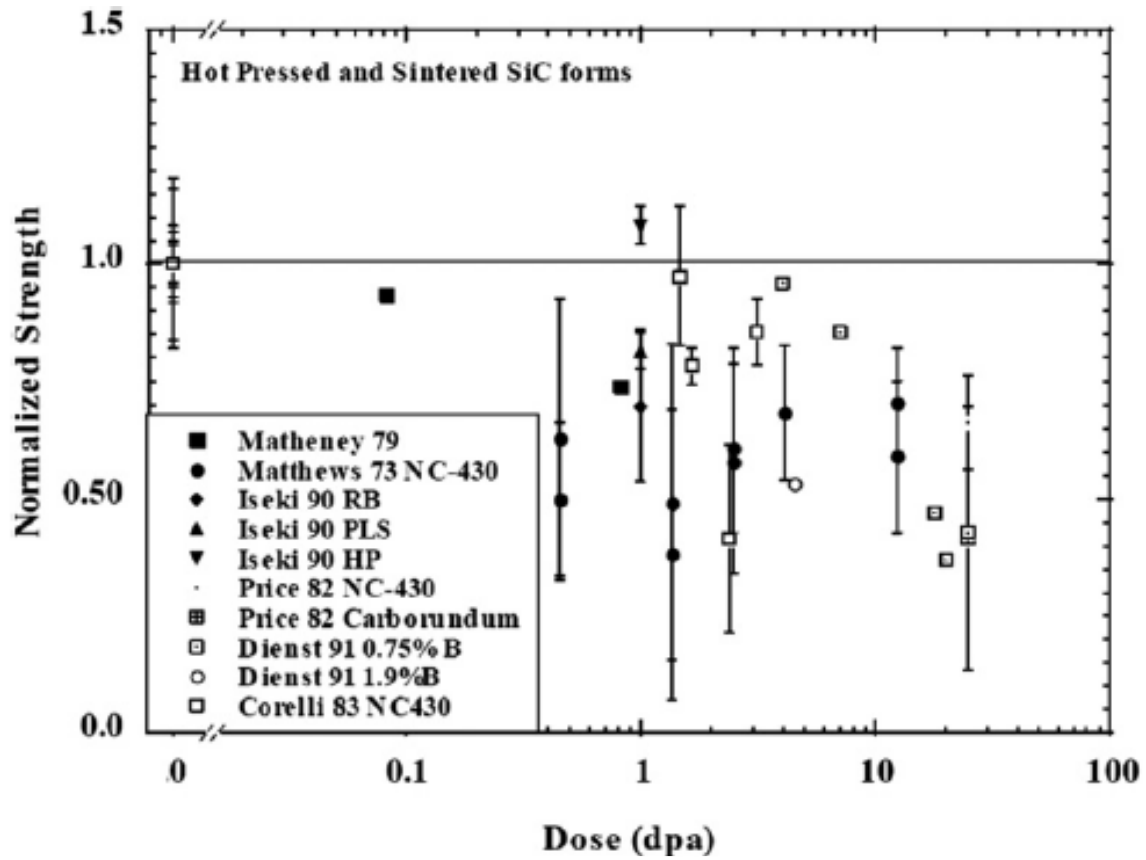


Figure 2.18: degradation of strength in HP and sintered SiC. Reprinted from the Journal of Nuclear Materials 371, L.L. Snead, T. Nozawa, Y. Katoh, T.S. Byun, S. Kondo, D.A. Petti, Handbook of SiC properties for fuel performance modeling, 329-377, Copyright 2007, with permission from Elsevier [21].

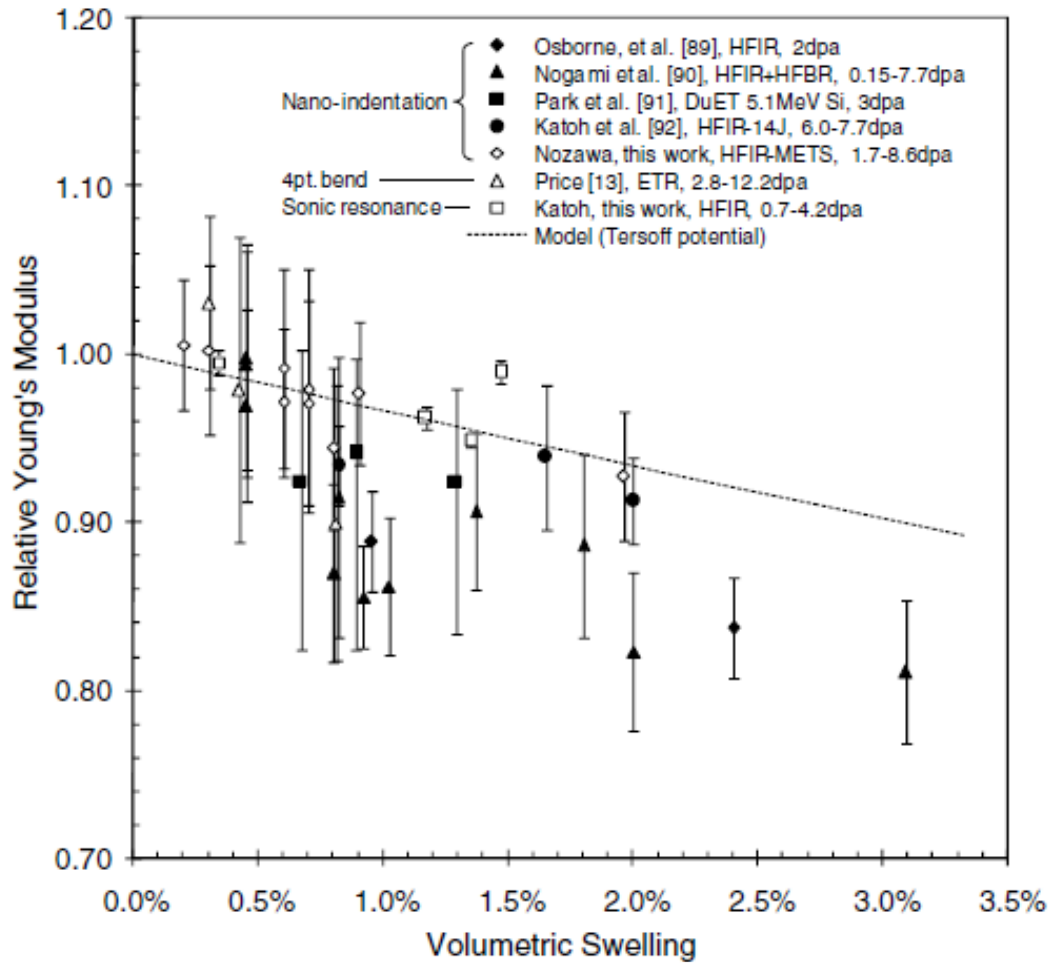


Figure 2.19: Correlation of elastic modulus degradation to swelling. Reprinted from the Journal of Nuclear Materials 371, L.L. Snead, T. Nozawa, Y. Katoh, T.S. Byun, S. Kondo, D.A. Petti, Handbook of SiC properties for fuel performance modeling, 329-377, Copyright 2007, with permission from Elsevier [21].

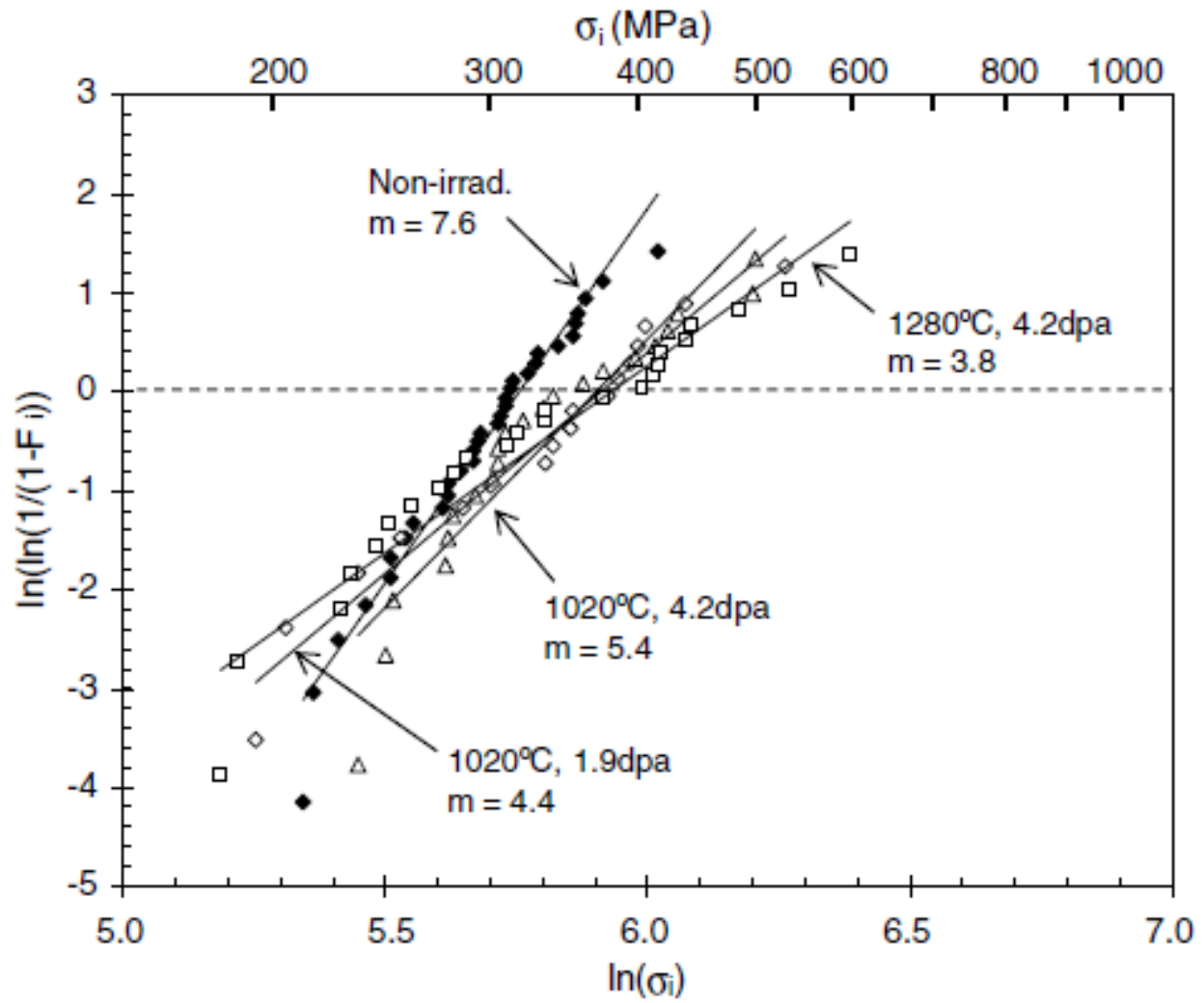


Figure 2.20: Weibull statistical parameters for tubular CVD SiC in unirradiated and irradiated SiC. Reprinted from the Journal of Nuclear Materials 371, L.L. Snead, T. Nozawa, Y. Katoh, T.S. Byun, S. Kondo, D.A. Petti, Handbook of SiC properties for fuel performance modeling, 329-377, Copyright 2007, with permission from Elsevier [21].

parameters are in reasonable agreement with the flexural data [21].

2.8.7 Thermal Conductivity Degradation

Thermal conductivity changes in SiC due to irradiation have been studied extensively [5, 21, 33, 37, 40, 42, 55, 68-70]. Fundamentally, thermal conductivity changes will follow the same time dependence as irradiation defects because these will cause phonon scattering and thereby reduce the conductivity (Figure 2.21 and Figure 2.22). Within the temperature range of interest for LWRs, the saturation of swelling as a result of point defect concentration saturation leads to an observed thermal conductivity saturation as well [5, 7, 21, 33, 37, 69, 70]. A linear relationship between swelling and conductivity for the LWR temperature range allows conductivity to be measured directly from swelling data (Figure 2.23) [5, 20, 37]. For CVD SiC, this leads to a thermal conductivity change from ~350 W/m-K to ~25 W/m-K at 800°C. Using HP SiC shows a similar saturation of conductivity with dose, but a lower (~90 W/m-K) thermal conductivity without irradiation.

High-temperature defect healing leads to a conductivity of 110 W/m-K in SiC irradiated at ~1600°C [21, 37]. However, the defect clusters which form more readily (voids) do not scatter phonons as individual defects or small clusters do, leading to a loss of the linear relationship between the conductivity and swelling, along with a loss of saturation of conductivity with dose [21]. As a result, under the void swelling regime (>1000°C), predictive models for the conductivity have yet to be developed.

2.8.8 Irradiation-Induced Creep

This phenomenon is most pronounced below ~1100°C, where thermally-induced creep is inactive due to a lack of supersaturation of vacancies. Irradiation provides this supersaturation, allowing dislocations to climb and therefore the material to creep [21, 37, 56, 71]. For 3C-SiC, creep becomes strongly nonlinearly dependent on irradiation damage above 0.7 dpa, and then saturates at rather low values (creep compliance estimations are about 2.7×10^{-7} /MPa-dpa and 8×10^{-5} /MPa-dpa for 600-1000°C and 1100°C, respectively for the close-packed direction) [21, 37]. Until vacancies become mobile, near 1100°C, creep appears to be dominated by defect rearrangement in the material. Above 1100°C, vacancies are mobile and metallic creep mechanisms become important [21, 72]. Extensive data is not available for irradiation creep on SiC but is very important to the determination of viability over at least a 5-year period of a service for fuel rods in a nuclear environment. However, the given estimates of irradiation creep predict that under standard LWR conditions, creep will be <<0.1%, the lowest expected value of point-defect swelling in SiC, assuming 10^{-6} dpa/s and a constant applied stress of 20 MPa, making irradiation creep irrelevant for LWR ATF cladding [40].

2.9 Corrosion Characteristics

This section describes the various considerations and data surrounding LWR corrosion of SiC. While much work has been done on corrosion of SiC in a variety of environments, only LWR conditions are considered, for brevity.

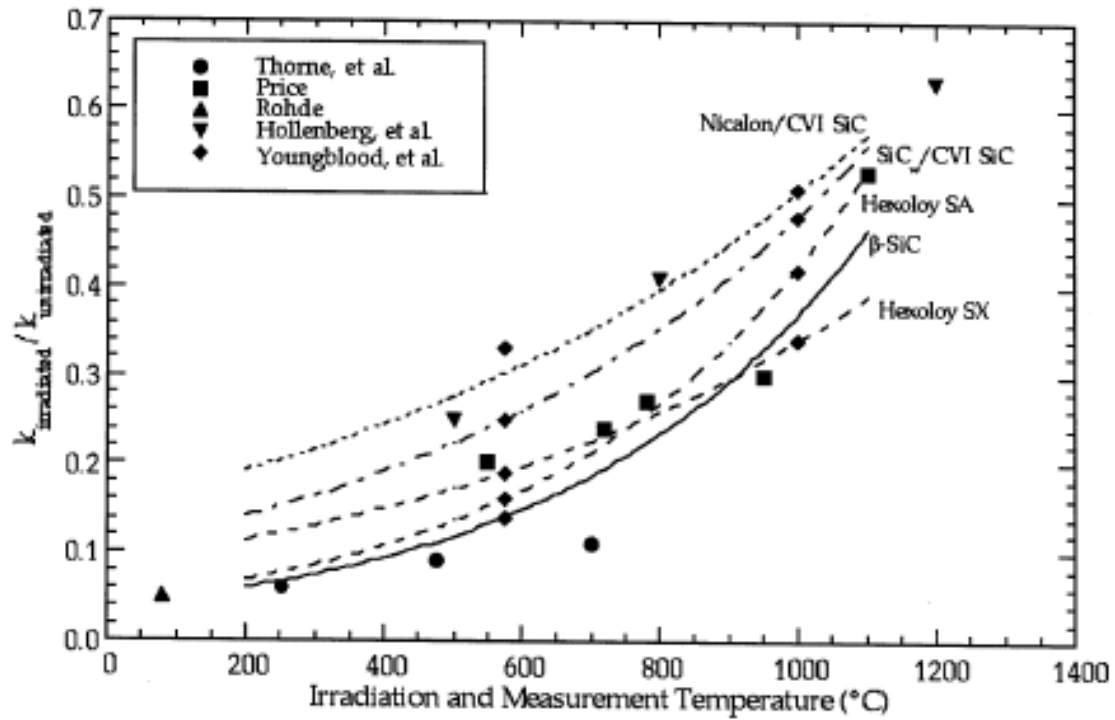


Figure 2.21: Thermal conductivity ratio of irradiated to unirradiated SiC as a function of temperature. Even to high temperature, substantial degradation is noted. Reprinted from Fusion Engineering and Design, 55, A.R. Raffray, R. Jones, G. Aiello, M. Billone, L. Giancarli, H. Golfier, H. A., Y. Katoh, K. A., S. Nishio, B. Riccardi, M.S. Tillack, Design and material issues for high performance SiCf/SiC-based fusion power cores, 55-95, Copyright 2001, with permission from Elsevier [69].

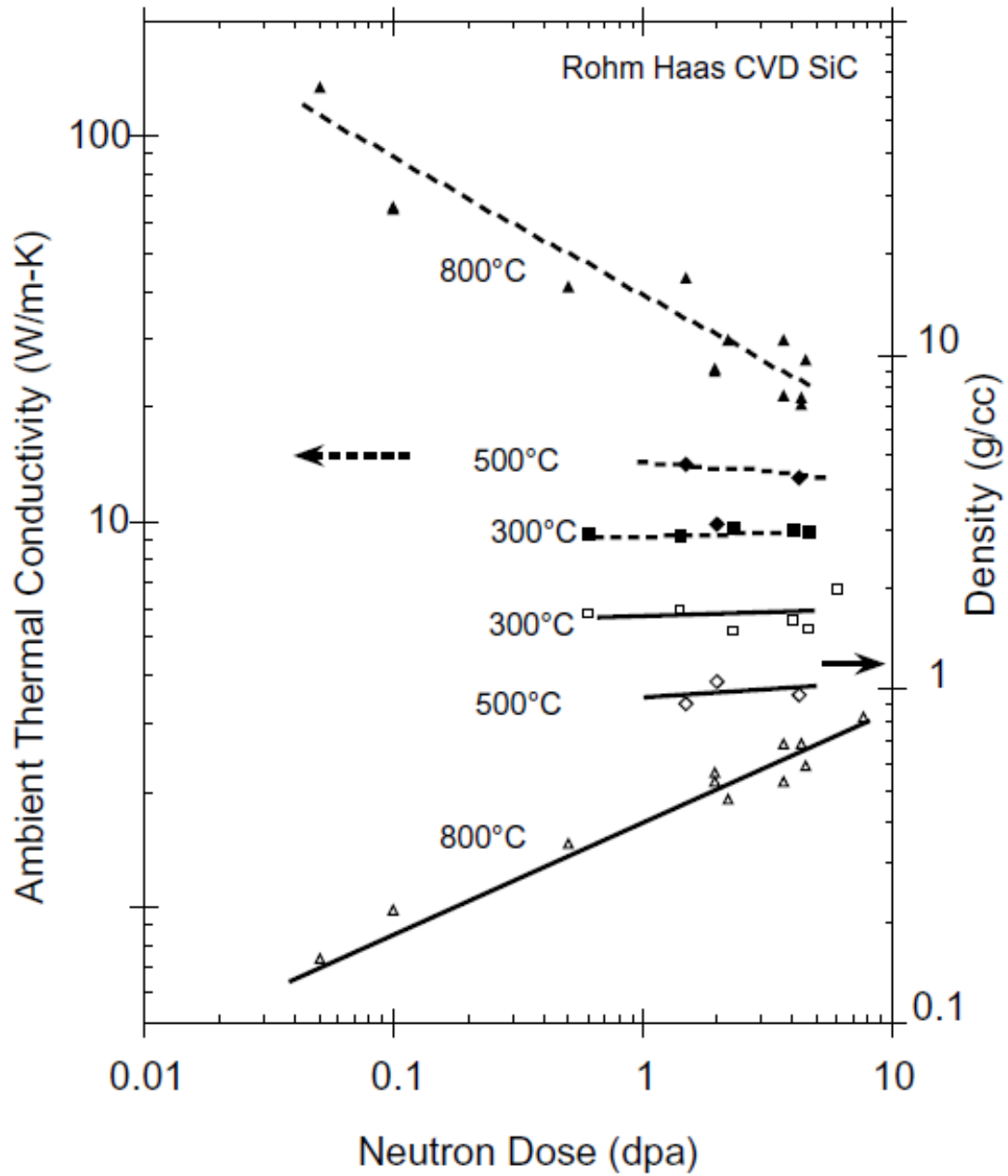


Figure 2.22: Conductivity and density dependence of CVD SiC on neutron dose. Irradiations performed in HFIR (High Flux Isotope Reactor). Reprinted from the Journal of Nuclear Materials, 329-333, L.L. Snead, Limits on irradiation-induced thermal conductivity and electrical resistivity in silicon carbide materials, 524-529, Copyright 2004, with permission from Elsevier [73].

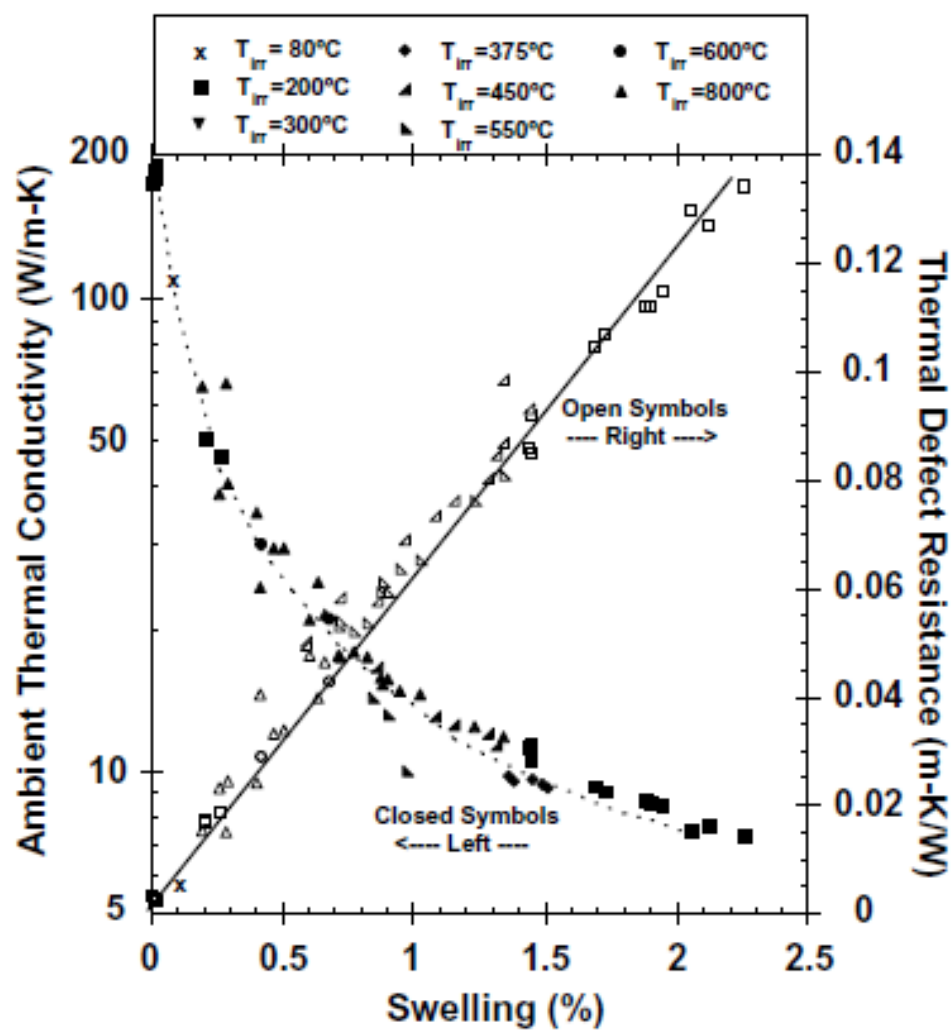
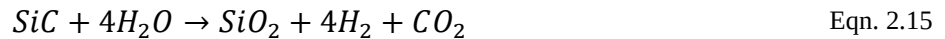


Figure 2.23: Thermal conductivity mapping to swelling showing linear increase in thermal defect resistance to swelling for irradiation in the lattice swelling regime (200-1000°C). Reprinted from the Journal of Nuclear Materials 371, L.L. Snead, T. Nozawa, Y. Katoh, T.S. Byun, S. Kondo, D.A. Petti, Handbook of SiC properties for fuel performance modeling, 329-377, Copyright 2007, with permission from Elsevier [21].

2.9.1 Chemistry of SiC reactions with Air and Water

Oxygen and water are thermodynamically favored to react with SiC to react via the following reactions [5, 11, 14, 21, 46, 74-80] which are all spontaneous at the temperatures of interest for LWRs per data from [81].



Of all studies conducted on the corrosion of SiC, the vast majority have focused on either corrosion in air or steam especially within the nuclear energy community [21, 82-90]. Under purely oxygenating environments (no water or steam), SiC reactions are completely described by Eqn. 2.9-Eqn. 2.11 with different reactions dominating depending on the oxygen partial pressures and temperatures [21, 56]. Formation of SiO₂ leads to an amorphous passive adherent scale below 1673 K, which serves to protect the underlying SiC after initially large mass gain; these reactions are termed “passive oxidations” for this reason [21, 56]. Increasing scale thickness requires longer paths for O₂ diffusion, and thus decreased reaction rates over time, leading to parabolic corrosion kinetics. Intuitively, impurities in the SiC matrix will increase the corrosion rate by aiding in diffusion through the SiO₂ film [21].

Active corrosion occurs when the SiO₂ layer cannot be formed Eqn. 2.8. In dry gas environments, this occurs when O₂ partial pressures are low. The specific transition concentration from active to passive corrosion varies several orders of magnitude depending on the impurity concentrations of the SiC variant [21]. Other mechanisms pertinent to LWRs that remove the oxide or prevent its formation are discussed in the following sections 2.9.2 and 2.9.1. Under active corrosion in CMCs, there is an additional mechanism of interface removal (IRM), which preferentially degrades fiber interfaces, potentially leading to fiber fallout, and decreasing the crack mitigation effects of the fibers [41, 51].

2.9.2 Hydrothermal Corrosion under Normal Operation in LWRs

Corrosion of SiC under normal LWR operating conditions has been reported to be potentially too large for fuel cladding applications [5, 11, 14, 15, 44, 51, 91]. A protective SiO₂ layer is unable to form due to its chemical reaction in water per the following dissolution mechanism, Eqn. 2.16, leading to linear, active, corrosion rates [11, 14, 51, 74, 76, 80, 92-94]. Hirayama et al [74]

reported that the film may also dissolve by producing H^+ and SiO_3^{2-} , implying that higher pH values would drive the reactions towards dissolution. However, that study used impure sintered SiC creating some uncertainty in the results compared to high purity CVD SiC. Corrosion further tends to occur at grain boundaries in oxygenated conditions as reported extensively (Figure 2.24, although there is some evidence to suggest that lack of oxygen and a highly-crystallized SiC specimen can suppress grain boundary attack [92, 93]) [5, 11, 80, 91, 93-95], at least some of which is likely caused by initial oxidation of grain boundaries prior to autoclave testing [39]. Some pitting on grain boundaries has also been observed at the beginning of grain boundary attack [94]. If corrosion takes place over the course of weeks to months with sufficiently high temperatures and oxygen contents, this can also lead to grain fallout [25, 91, 93, 96].



Recent simulation work by Liu et al examined attack of SiC by O_2 at 2000K using Molecular Dynamics (MD) tools [97]. They found that grain boundary attack is expected at all incoherent grain boundaries as a consequence of the dangling bonds (and free Si and C) at the boundary. Coherent grain boundaries were not expected to corrode faster than the bulk SiC.

Because O_2 is a major factor in SiC corrosion, additions of H_2 to the water to scavenge oxygen significantly reduces the rate of corrosion as demonstrated in Figure 2.25 and reported by a number of authors. Terrani et al used this data to roughly estimate a corrosion activation energy in the absence of oxygen to be about 18 kJ/mol [11] (It should be noted that Terrani et al. agreed that this number is highly uncertain since it compared only two conditions where the pH was not common between them). This effect is exacerbated for non-CVD processing techniques which increase the grain boundary corrosion rates by impurity segregation [5, 15, 24, 25, 92, 93, 95, 98, 99] as illustrated below in Figure 2.26. Moreover, fiber-matrix interfaces in composites lead to significant increases in the corrosion rate for CMCs over pure specimens [92].

Further, there is evidence that low resistivity SiC may degrade more quickly. Shin et al. [100] investigated PWR-simulating water at 360°C for up to 90 days. They found that increasing the resistivity had a substantial impact on the uniform corrosion rate, also dramatically increasing the grain boundary attack. This is shown in Figure 2.27.

The effects of irradiation on the corrosion of SiC have not been well studied. Kondo et al. [91] tested specimens pre-irradiated up to an average 2.6 dpa with 5.1 MeV Si ions and saw full removal of the irradiated region (past the implantation depth). While the authors conclude that irradiation greatly accelerates corrosion, it is equally likely that the unirradiated/irradiated interface were accelerated due to the swelling stresses, leading to fallout of the region, rather than chemical removal. More work is needed to determine any effects of corrosion, but Kondo's work implies that some increase is likely to be observed.

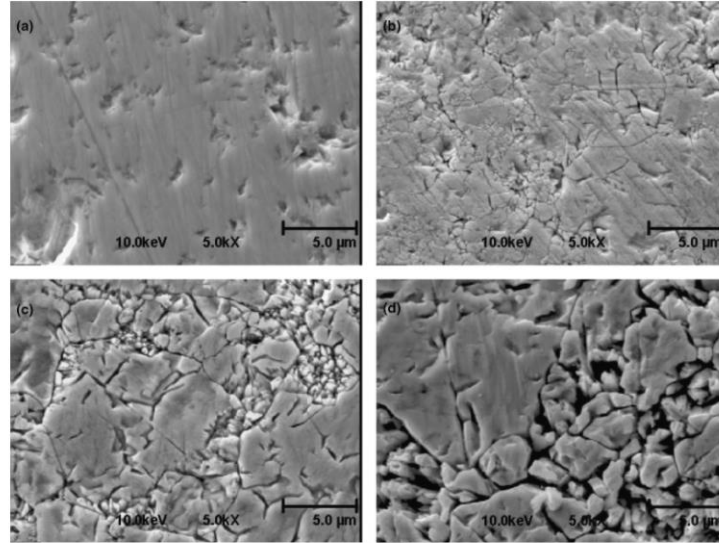


Figure 2.24: Corrosion of grain boundaries in R&H CVD SiC. a) is as received sample, b), c), and d) are the same sample after 7, 14, and 21 days in 500°C deoxygenated supercritical water. Similar data for compressed water under LWR conditions is found in [91]. This figure is reprinted from Journal of Nuclear Materials 464(Supplement C), S. Kondo, M. Lee, T. Hinoki, Y. Hyodo, F. Kano, Effect of irradiation damage on hydrothermal corrosion of SiC, 36-42, Copyright 2006 the American Ceramic Society, with permission from Wiley [93].

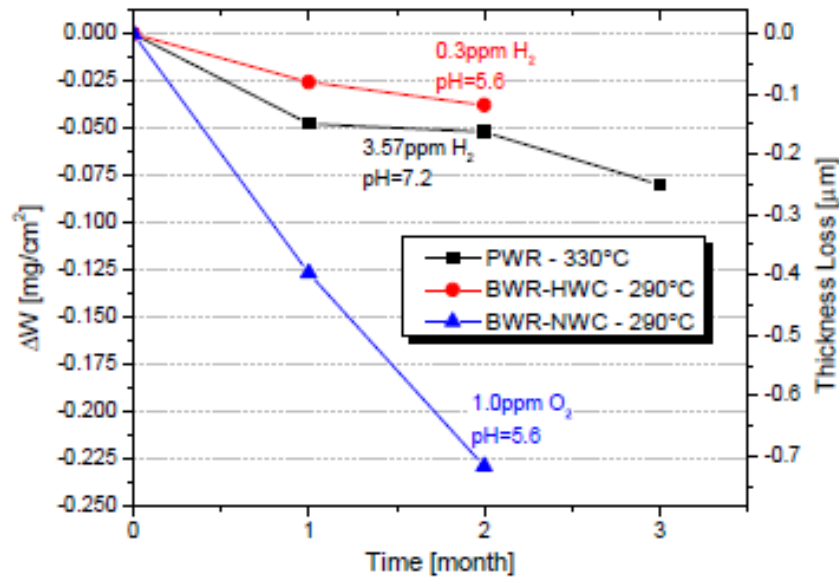


Figure 2.25: Comparison of the corrosion rate of standard CVD-SiC in the three LWR chemistries. Similar data can be found in [5, 80]. Reprinted from the Journal of Nuclear Materials, 465, K.A. Terrani, Y. Yang, Y.J. Kim, R. Rebak, H.M. Meyer, T.J. Gercozak, Hydrothermal corrosion of SiC in LWR coolant environments in the absence of irradiation, 488-498, Copyright 2015, with permission from Elsevier [11].

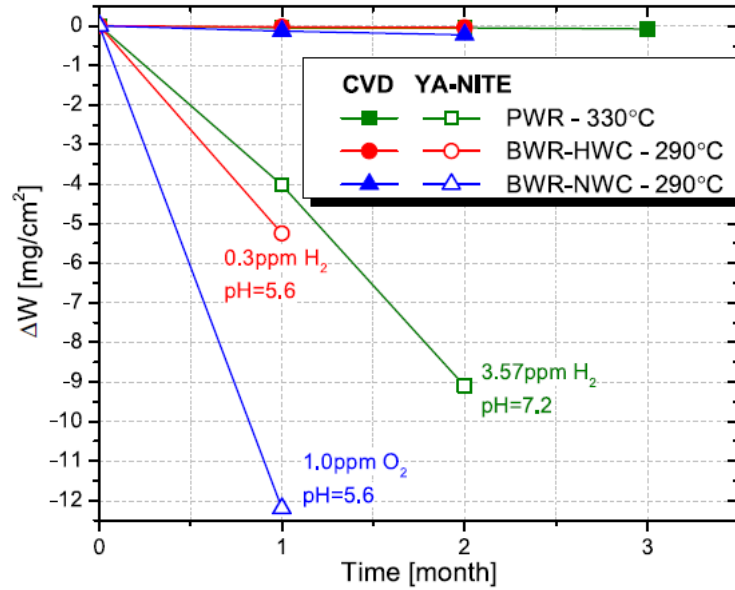


Figure 2.26: Difference between hydrothermal corrosion of CVD and NITE processed SiC. Reprinted from the Journal of the European Ceramic Society, 37, C.M. Parish, K.A. Terrani, Y.-J. Kim, T. Koyanagi, Y. Katoh, Microstructure and hydrothermal corrosion behavior of NITE-SiC with various sintering additives in LWR coolant environments, 1261-1279, Copyright 2017, with permission from Elsevier [15].

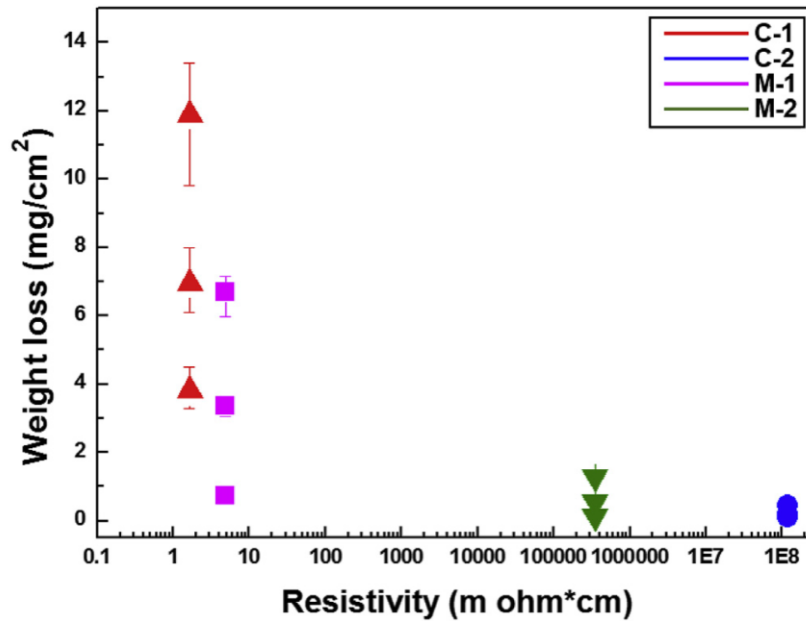


Figure 2.27: Comparison of the corrosion rate of various CVD SiC specimens exposed to PWR-simulating water at 360°C and 18.5 MPa pressure for 30, 60, and 90 days (corresponding each of the three points low to high mass loss, respectively, on the plot). Reprinted from the Journal of Nuclear Materials, 518, J.H. Shin, D. Kim, H.-G. Lee, J.Y. Park, W.-J. Kim, Factors affecting the hydrothermal corrosion behavior of chemically vapor deposited silicon carbides, 350-356, Copyright 2019, with permission from Elsevier [100].

2.9.1 LOCA Corrosion

Under LOCA conditions, Eqn. 2.16 proceeds slowly enough that corrosion is impeded by formation of a SiO_2 film which remains intact if the flowrate of steam is not excessive [75, 77, 101-103]. For shorter exposure times, the film is observed to be highly porous and non-passivating, whereas longer exposure results in an underlying dense silica layer, with a porous layer ontop [77]. The observed corrosion rates are low enough that SiC is a viable cladding material for LOCA conditions, as shown in Figure 2.28. In this regime an activation energy of about 150-200 kJ/mol (about 10 times the activation energy for corrosion under normal operation without oxygen) has been reported [103]. Moreover, there is some indication that the SiO_2 film does not protect fibrous SiC under these conditions [103].

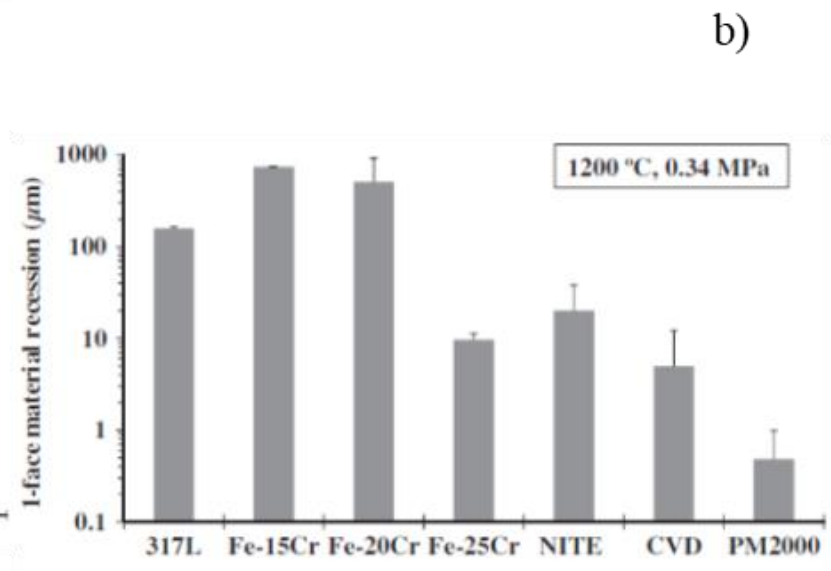
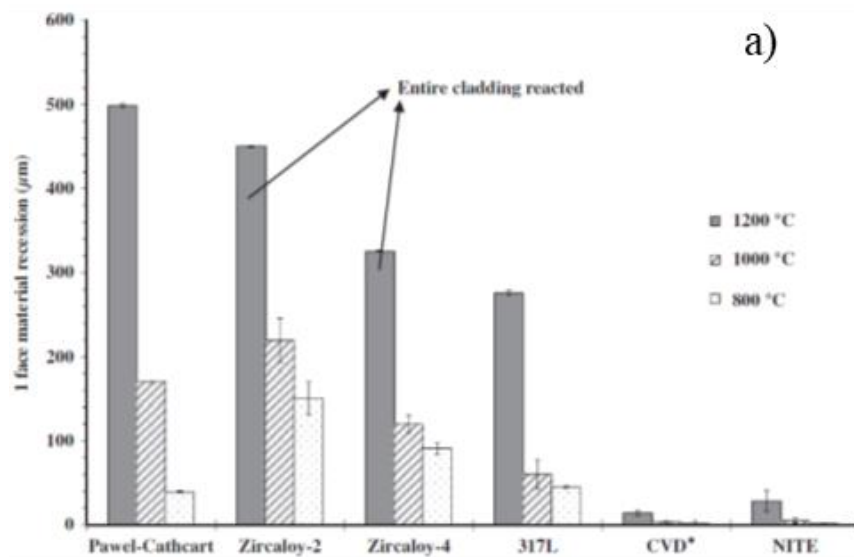


Figure 2.28: Performance of various LWR fuel cladding materials under LOCA conditions. a) comparison of SiC corrosion to steel and Zircaloy at various temperatures. b) comparison of a variety of ATF candidate clads. Both show superiority of both FeCrAl and SiC to other cladding options. Reprinted from Journal of Nuclear Materials, 427, T. Cheng, J.R. Keiser, M.P. Brady, K.A. Terrani, B.A. Pint, Oxidation of fuel cladding candidate materials in steam environments at high temperature and pressure, 396-400, Copyright 2012, with permission from Elsevier [102].

Chapter 3: Experimental Methodology

This work was divided up into three main parts. Different scoping studies (section 3.1) were performed at both General Electric's (GE) and ORNL's hydrothermal corrosion laboratory (HCL). These were intended to reproduce expected results from literature (see Chapter 2), and evaluate the qualitative viability of specific mitigation coatings, which section 3.1 describes. From the scoping results, a number of studies were designed to obtain more robust corrosion information for monolithic and coated SiC within the temperature range of interest with a focus on fundamental corrosion science (section 3.2). Finally, a large irradiation campaign was performed at MIT's nuclear reactor (section 3.3), of which monolithic and coated SiC was a portion of the test matrix. This campaign was designed to evaluate corrosion under radiolysis with and without irradiation damage, corrosion without irradiation (for comparison) and dry irradiation. The detailed experimental conditions of these studies are discussed below. Following the discussion, a table is given summarizing all sample information. The information in this and chapters 4 and 6 can be found in [14, 51, 104-109].

3.1 Scoping Studies

3.1.1 Corrosion of basic specimens at General Electric (GE)

The first set of scoping studies was planned by Kurt Terrani (ORNL) and the corrosion carried out by Raul Rebak (GE) at the GE Global Research Center (Schenectady, NY). The author planned and carried out all post-corrosion characterization, which is reported in Doyle et al, [14]. Due to the corrosion rates observed by Terrani et. al. [11], four different types of monolithic SiC were used, each quoted to a purity of >99.9995% SiC. Individual impurities were not independently verified. SiC variants consisted of high resistivity (HR) and low resistivity (LR) SiC from Coorstek (Oak Ridge, TN), a high resistivity equivalent (HHT) from Rohm and Haas (R&H, Deer Park, TX), and 4H single crystal from University Wafer (UW, South Boston, MA). The two high electrical resistivity variants were high purity CVD SiC from different vendors. Both were included in order to study the impact of variations in processing. All three of these were polycrystalline, leading to the expectation of increased mass loss via grain boundary attack (see Chapter 2). The single crystalline SiC was included to provide a baseline without any grain boundary attack.

Fused SiO₂ and single crystal Si from UW were also included. SiO₂ was important to validate that the reaction of SiC to form SiO₂ is the rate limiting step as expected from literature (see Chapter 2). Faster dissolution of SiO₂ relative to SiC was expected to confirm this. Si is a common impurity in the state-of-the-art RB techniques, and has been implicated as the cause of excessive corrosion in that material. Pure Si was included as a check on literature data. Single crystal and polycrystalline alumina from UW and Coorstek were included due to their necessity for sufficient density in the sintered processing variants of SiC (see [15]).

Coupons were exposed in a 3.8 L type 316 stainless steel autoclave with constantly-refreshing water at GE Global Research Center. Water chemistries simulated PWR, BWR-HWC, and BWR-NWC conditions, see Table 3.1 (Table 3.2 shows similar conditions for the ORNL tests, section 3.2, and Table 3.3 shows the conditions for corrosion at the MIT reactor, section 3.3). No

Table 3.1: Specific water chemistry conditions for the PWR, BWR-NWC, BWR-HWC tests at GE and the BWR-NWC, BWR-HWC tests at the ORNL HCL

Condition Designation	Gas Conc. (ppm)	Temperature (°C)	pH¹	Pressure (MPa)
<i>PWR</i>	3.57 H ₂	330	5.8	15
<i>BWR-HWC</i>	0.3 H ₂	290	5.6	7.5
<i>BWR-NWC</i>	1.0 O ₂	290	5.6	7.5

Table 3.2: Specific water chemistry conditions for all tests at ORNL. Both pH and electrochemical potential (vs the standard hydrogen electrode (SHE)) were determined with FactSage7.2TM for the given conditions.

Condition Designation	Gas Conc. (ppm)	Temperature (°C)	E_{SHE} (V)	pH¹	Pressure (MPa)
<i>Set 1 (NWC)</i>	2.0 ppm O ₂	288	0.35	5.6	10
<i>Set 2 (HWC)</i>	150 ppb H ₂	288	-0.53	5.6	10
<i>Set 3</i>	2.0 ppm O ₂	320	0.27	5.7	15
<i>Set 5 (PWR)</i>	3.0 ppm H ₂	320	-0.64	5.7	15
<i>Set 6</i>	150 ppb H ₂	350	-0.58	5.7	19
<i>Set 8</i>	1.0 ppm O ₂	350	0.19	5.7	19
<i>Set 4</i>	2.0 ppm O ₂	350	0.20	5.7	19
<i>Set 9</i>	4.0 ppm O ₂	350	0.21	5.7	19

Table 3.3: Water chemistry of the MIT reactor test. Electrochemical potential versus SHE was calculated

Condition Designation	Gas Conc. (ppm)	Temperature (°C)	E_{SHE} (V)	pH	Boron/Lithium (ppm)	Pressure (MPa)
<i>MIT</i>	4.2	300	-0.84	6.6	1200/4.3	10.3

¹ pH is calculated using the FactSage7.2TM equilibrium tool. Similar values are obtained using the K_w of pure water at the given temperature and pressure as determined using [110] C.A. Meyer, R.B. McClingtock, G.J. Silvester, R.C.J. Spencer, 1967 ASME STEAM TABLES, 2 ed., The American Society of Mechanical Engineers, New York, NY, 1967, [111] W.L. Marshall, E.U. Franck, Ion product of water substance, 0–1000 °C, 1–10,000 bars New International Formulation and its background, Journal of Physical and Chemical Reference Data 10(2) (1981) 295–304.

boric acid or lithium hydroxide were added to the PWR system. While these are important additives to achieve the actual operating pH, they contaminate the entire autoclave system, so dedicated boron and lithium loops need to be used for these studies. Additionally, the pH of the three simulated systems is quite similar without the boron and lithium adjustments, making comparison of the data more straightforward. One sample was used per exposure condition, for each sample type. Samples were exposed for three months and were removed at the end of each month to measure mass loss. Mass loss on each sample was reported as the average of three measurements. Each measurement had an accuracy of 0.001 mg with an average precision of 0.02 mg.

Following all tests, they were transported to ORNL, where they were cleaned for 5 minutes in acetone, 5 minutes in methanol, and 3 minutes in ethanol in order to remove any non-adherent products. After cleaning each was dried with a Kim wipe and placed in a clean bag. Each sample was examined with SEM using the Hitachi S4800 for high resolution images and some EDS mapping. The Hitachi S3400 was used for some lower resolution images with quick EDS mapping. Following SEM, samples were examined by Raman using a LabRAM HR Evolution Raman Spectrometer by Horiba Scientific using a 532 nm laser with a spot size of ~40 microns. Raman was chosen because it is an excellent, quick spectroscopic technique for identifying the chemical makeup of a specimen. The monochromatic laser interacts with each molecule in the system by exciting/de-exciting electrons to higher or lower energy levels through elastic scattering of the light. The light coming off of the specimen is thus shifted to a higher or lower wavelength based on the energy it deposited (due to excitation of electrons) or absorbed (as an electron decreased in energy). The local chemical environment of each element determines the magnitude of the shift and the size of the peak distribution. In complex chemical systems Raman is complementary to Infrared Spectroscopy (IR) because each examines different aspects of the molecule. IR is sensitive to the vibrational modes of a bond, while Raman is sensitive to bond polarizability. For this study, because both compounds of interest, SiO₂ and SiC, are sensitive to Raman, only Raman was performed.

3.1.2 Corrosion of pure and coated SiC at the Hydrothermal Corrosion Lab (HCL) at ORNL

For the second part of the scoping studies, the results of the first scoping tests (see Chapter 4) were used to specify a variety of coatings for potential application to protect SiC. These were developed by Caen Ang as part of a post doctorate appointment with Kurt Terrani and Yutai Katoh at ORNL. Extended details of the coating processes and choices can be found [112]. Reasons for each choice are given below. All samples were tested at the ORNL HCL. Testing was performed in simulated BWR-HWC and BWR-NWC conditions. Parameters for these tests were the same as in Table 3.1 with gas concentrations monitored by bubbling of gas through a column kept an overpressure of ~1 atm, BWR-HWC was achieved with a bubbling gas concentration of Ar-4.6%H₂. To obtain BWR-NWC, a concentration of Ar-5%O₂ gas was bubbled at atmospheric pressure with the same autoclave pressure. Temperature was controlled with a PARR Reactor Controller #4838 with continuous data monitoring and recording by a LABVIEW program created by Adam Willoughby, an ORNL technician. Conductivity and temperature readings were recorded manually every few minutes at startup until equilibrium was

achieved and periodically during normal operation. Schematic layout and images of the loop can be found below in Figure 3.1 and Figure 3.2, respectively.

The system normally took ~2 hours to fully heat, and ~2 hours to cool below 200°C, making the error in test time below 4 hours. The BWR-NWC test consisted of two 200 hour increments for a total of 400 hours of testing. The BWR-HWC test consisted of one 200 hour test, one 50 hour test, and one 150 hour test, for a total of 400 hours. The extra test time increment was caused by a substantial leak during the 50 hour test period which necessitated loop shutdown. A final increment of 150 hours was added to reach the 400 hour mark. Errors in test time estimation are thus suitably small to not affect calculated corrosion rates. To ensure the flow rate was sufficient, inlet and outlet conductivity were monitored. Inlet conductivity never increased above 0.1 $\mu\text{S/m}$, and outlet conductivity typically remained below 0.1 $\mu\text{S/m}$ during the bulk of the test. Although at the beginning of the test it increased somewhat above 0.2 before settling down below 0.1.

Because these were scoping studies, 400h was considered sufficient to disqualify clearly unsuitable coatings, with longer, more thorough tests planned for the remaining sample types. No PWR tests were performed during the scoping section for two reasons. First, it is expected that the PWR conditions will simply be a little more aggressive than the BWR-HWC due to the temperature increase. Since no boron or lithium is in the system, no additional chemical aggressiveness is expected beyond the temperature. Thus, a lower bound to disqualify coatings is established with the two conditions given. Second, the loop was not fully equipped for PWR analysis initially. The pressure vessel was designed as a batch reactor, not a continuously flowing reactor. Thus, it was unable to heat the system above 300°C while maintaining the required flowrate. Moreover, the gas delivery system was not initially able, for safety reasons, to carry pure or nearly pure H_2 , as is required to achieve the dissolved hydrogen levels needed for PWR testing. These problems have since been rectified.

The BWR-NWC and BWR-HWC tests contained similar specimen types, although a few more were contained in the HWC test as explained below. Both contained one of each CVD SiC (R&H) coated with either ZrN_{1-2} (Oerlikon Balzers Coatings, OB), Cr (Richter Precision, RP), TiN (Techmetals, TM), CrN (RP), or Ni (ORNL), NiCr (ORNL), along with uncoated Hypertherm CMC SiC, NGNP (Next Generation Nuclear Plant) CMC SiC with Hi-Nicalon S fibers, TiN with 1wt% Ni (Coorstek), Cr (ORNL), Ni-200, and unpolished CVD SiC (R&H). Each of these coatings was chosen by Caen Ang for testing based on potential suitability for LWR applications and after vetting of the candidates based on physical and microstructural properties. ZrN is attractive from a neutronics standpoint and industry familiarity with Zr. Cr forms an adherent, passivating oxide at operating temperatures, can be coated very thinly on the surface of SiC, but has a high thermal neutron cross section. CrN has a lower thermal neutron cross section for absorption (due to the excess nitrogen). Ni can also form a passivating oxide and once electrolessly coated on a specimen. The high conductivity of Ni allows electroplating of additional coating layers to be used as the coating process, rather than the expensive and time-consuming PVD process currently required due to the low conductivity of pure SiC. NiCr follows directly from the benefits of both Ni and Cr, which are also taken advantage of in stainless steels. Additional coating types manufactured by ORNL/NEO industries were prepared

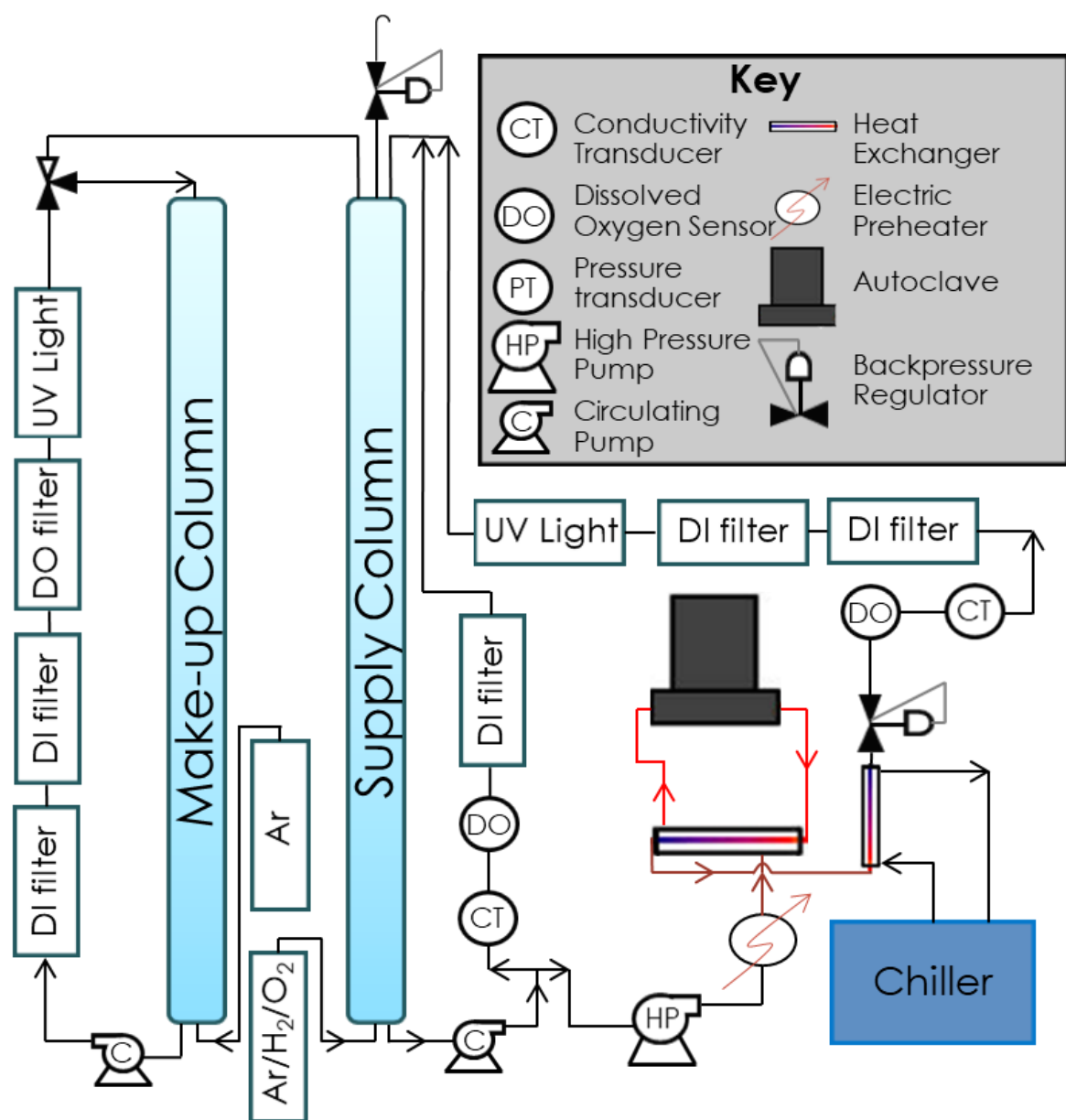


Figure 3.1: Schematic layout of the HCL loop. Only the 3.8L autoclave was used for these tests.



Figure 3.2: Images of the HCL water loop (excluding the DI water section) with Dr. Stephen Raiman and the author operating the loop.

by electroless coating of the SiC substrate with Ni, followed by electroplating of the desired coating type. These coatings were not ready as of this set of tests, and were disqualified following them as not being adherent enough for corrosion testing so only the PVD coatings were included. The CMCs were added for reference to the CVD SiC, which was added for comparison to literature. The other pure materials were added to provide a basis to compare to coatings for validation of whether the coating or its substrate was corroding. The TiN was not theoretically dense as discussed in Chapter 4. The addition of Ni was required during sintering to obtain the material finally used. Further details of the coating methods and properties are found in Caen et al. [112].

3.2 Unirradiated Corrosion Studies at the HCL

Eight different exposure conditions were explored as part of the more extensive studies. The standard LWR conditions, BWR-NWC, BWR-HWC, and PWR were used for a baseline to other tests and to make this work directly applicable to industry. Additional tests were added to properly identify the rate constants, which of the chemical reactions with oxygen is dominant (i.e., the reaction order with respect to oxygen), and the dependence on temperature (and thereby the various relevant activation energies). All conditions are given in Table 3.2. No Li or B were added to the PWR test as the loop is not set up for those additions. The oxygen and hydrogen conditions specified were chosen based on those currently used across the three LWR systems. The temperature ranges were similar, but the final temperature of 350°C, was chosen to provide an upper limit before the water critical point.

Several candidate coatings were disqualified during the second part of the scoping tests at the HCL. Details can be found in section 4.1.4 and 6.2.3. The remaining coating types for extensive testing were Cr, CrN, and TiN. The Cr and the multilayer Cr/CrN coating, with thicknesses of approximately 4.5 and 14µm, respectively, were manufactured by Richter Precision (RP) via a proprietary PVD method. Another nominally monolithic CrN (~8.5µm thick) with ~10 nm Ti compatibility coating and the TiN (~3µm thick) coatings were manufactured by Techmetals (TM) via a proprietary PVD method. Two coating vendors were used for CrN, because it did not perform as well as the others in the scoping tests, and Cr layers dispersed through the coatings for crack mitigation was desirable. Coating stoichiometry was determined by an outside company, EAG, using x-ray photoelectron spectroscopy (XPS) and is reported in Table 3.4.

Each test contained three of each coated SiC specimen so that experiment error would be quantifiable. Due to limited number of samples, only 1 sample of each type was included in the 350°C and 150ppb H₂. Reference monolithic ceramic coating materials were too porous and were sintered, thus not properly representing the materials as a reference. Thus, no reference samples are reported on following the scoping tests.

The first set of scoping studies (section 3.1.1) was not able to quantify the extent of grain boundary attack on SiC (see Chapter 4). Moreover, a primary objective of the present study was to determine the corrosion kinetics of SiC. To evaluate both these aspects, a total of six pure SiC samples were included with each test. Three of these were polished for EBSD both to remove the additional roughness (for comparison to as-cut surface) and for EBSD and AFM imaging to quantify grain boundary attack as a function of grain size and misorientation angle. Specifically,

Table 3.4: Stoichiometry of coatings as determined by XPS.

<i>Coating Type</i>	<i>Coating Vendor</i>	<i>Coating Stoichiometry (atm %)</i>
<i>TiN</i>	Techmetals	Ti _{43.8} N _{51.2} C _{2.4} O _{2.6}
<i>CrN</i>	Techmetals	Cr _{60.6} N _{31.5} C _{5.2} O _{2.4}
<i>CrN/Cr (multilayer)</i>	Richter Precision	Cr _{53.4} N _{36.0} C _{6.1} O _{3.9}
<i>Cr</i>	Richter Precision	Cr _{89.2} O _{5.9} C _{3.2} N _{1.7}

they were mounted in non-conductive epoxy, ground with 220, 500, 800, and 1200 grit paper for 1 minute each under 25N force. After grinding, each was polished using 6 micron, 3 micron, 1 micron, and 0.5 micron diamond suspensions with between 20 and 30 N force applied for 8 minutes each. The final step was a 0.04 micron SiO₂ suspension polish for 24 hours. The samples were then broken out of the epoxy and cleaned. The sample was then remounted such that the opposing side was exposed, and the polishing procedure repeated, along with removal from epoxy and cleaning. The other three were left unpolished, as-cut from a large block of R&H CVD SiC at ORNL. As with the coated specimens, three samples were used so that a standard deviation of the mass change could be determined to evaluate experimental error. The difference between polished and unpolished samples enabled evaluation of the effect of surface roughness.

Both the polished and unpolished surface roughness were determined by AFM using an MFP-Infinity instrument at the Joint Institute for Advanced Materials (JIAM) using a HQ-300-Au probe from Asylum Research under tapping mode in air for topographic analysis. Detailed information on this probe is reported in Table 3.5. While many probes exist for AFM analysis this one was chosen due to its applicability to hard systems and reasonable cost. AFM is well-suited to this task, having resolutions that can be as good as imaging individual atoms on the surface. The specific probe tip and AFM system are not designed for atomic resolution, but the higher vibrational frequency and reflective coating allow for observation of nm-size features. Polished surfaces are not truly flat, and this resolution is more than sufficient to determine the roughness differences between the samples with good analysis of roughness increase due to corrosion. While some of this could be explored by laser profilometry, AFM is superior for this application because features of the highly-polished surface are smaller than the wavelength of light, at which point laser profilometry cannot give an accurate estimate. Moreover, each of the polished specimens in these tests was analyzed for grain boundary attack. In order for laser profilometry to quantify a recessed boundary, that boundary would have to open up several hundred nanometers and detailed correlation between specific grains would be much harder than with AFM, especially if attempting to analyze the fine-grain structure typical of CVD SiC. Thus, AFM was used for all samples.

In order to perform grain boundary attack analysis, fiducial marks were made on one side of each as-polished sample in the oxygenated conditions. The marks consisted of a series of indents made by applying 50g-worth of force for 10 seconds using a Wilson TukonTM 1102 hardness indenter. Lower indenting forces made indents which were far too small to quickly locate in an SEM, while larger forces created extensive cracks from the corners of the indents. Indents were arranged into an “L” shape with an identifier mark. Each mark was made near an edge or corner for quick identification, and the length of each side of the “L” was typically greater than 100 microns. Thus, several hundred grain boundaries were available for recession analysis at each analysis condition. Following indentation, samples were lightly cleaned with acetone or methanol and wiped clean with a Kim wipe followed by air dusting to remove any residual surface artifacts. AFM scans of each region were performed using a target voltage of 1.0 V and an offset of -5% to create stronger contact with between the surface and tip. Since SiC is substantially harder than Si, the tip material, no scratching of the sample surface was expected to result, and none was observed (see Chapter 4). Specific voltage setpoints varied between

Table 3.5 Operational data for the HQ-300-Au probes from Asylum Research [113].

<i>Property</i>	<i>Value</i>
<i>Frequency (kHz)</i>	200-400
<i>Spring constant (N/m)</i>	20-75
<i>Length (μm)</i>	115-135
<i>Width (μm)</i>	32-34
<i>Thickness (μm)</i>	3.4-5.4
<i>Shape</i>	Rectangular
<i>Reflex Coating (nm)</i>	Ti/Au (5/40)
<i>Tip radius (nm)</i>	<10
<i>Tip height</i>	11-17
<i>Tip Material</i>	Si
<i>Tip coating (nm)</i>	0

individual tips, but generally ranged between 500 and 750 mV. Analysis of the data was done entirely in Gwyddion 2.45 [114]. Obvious artifacts (Such as streaks) and all indents were masked so that only the actual expected surface was analyzed. To correct for slight sample tilt, a mean plane fit was applied and true versus projected area was calculated using Gwyddion's intrinsic functions. Even if the sample bowed slightly, the polishing method (mounting in epoxy) creates quite flat surfaces, especially over small (<100 micron) distances so a polynomial fit was not needed. Following corrosion, select AFM scans were performed over the same regions and grain boundary attack quantified by line profiles across the boundary. When significant grain recession was found, additional AFM scans were performed to quantify recession very accurately across many grain sizes, and misorientation angles. Identification of individual grains was accomplished using EBSD data collected on a JOEL 6500F SEM at the high temperature materials laboratory (HTML) at ORNL using the TEAMTM software version 4.4 and analyzing with the EDAX OIM AnalysisTM 7.

All EBSD images were taken on non-mounted samples, before corrosion, and after AFM. While the samples were carefully handled to avoid any damage to the surface that was not due to corrosion, normal handling can produce some damage. For these specimens such damage is unlikely to produce artifacts for two reasons. First, SiC is an extremely hard material, and does not readily scratch. Second, any damage is likely to take the form of straight scratches and will be readily identified as such in subsequent AFM scans, rather than as grain boundary corrosion, which follows the shape of the grain. Therefore, performing EBSD after AFM is not expected to cause difficulty. All EBSD images were taken with 250 nm step sizes at 20.0 keV and 70° tilt with working distances between 5 and 15 mm. No significant accuracy difference was noticeable within this working distance range. The time required to obtain EBSD data on all indents did not permit easily using a single working distance. The standard crystal data for SiC in the TEAMTM software was used for grain analysis.

Following EBSD, samples were thoroughly cleaned in acetone, dabbed with a Kim wipe, and weighed, followed by optical imaging on the Keyence MacroScope VR-3100. Weighing was done at this step so that in the unlikely event any damage was done to the samples during AFM or EBSD analysis, it would not show up as corrosion mass loss following exposure. Moreover, it is possible that optical imaging of the sample might add small particles from the imaging stage. However, since no mounting of the sample, either by clips (SEM) or carbon tape (AFM), was required, no damage was expected. Therefore, the most accurate weight was expected to be obtained directly after cleaning and before optical imaging.

Weighing was performed with all samples in a round-robin manner (each sample was weighed once before a second weight was obtained) with a minimum of three measurements per sample on a Mettler Toledo XP-205 balance. All samples, coated, uncoated, and polished were weighed together so as to maximize the time between a single sample was weighed and then re-weighed, and therefore ensure no data points were correlated. No samples were put into the autoclave before validating by three or more repeated measurements that the mass was stable. An average of three or four consecutive data points was reported as the true mass of the sample along with

the standard deviation of the measurement. Standard deviations were typically between 0.01-0.02 mg, with a reported resolution by the instrument of 0.01 mg.

Following each exposure, the samples were removed, cleaned in acetone, allowed to air dry and then weighed in the same round-robin technique, followed by optical imaging. This ensured that any instabilities in the mass were readily determined and a good mass measurement obtained for each sample. For grain-boundary recession, the polished samples were then taken and scanned with AFM. Following this, they were re-cleaned with acetone and re-weighed to ensure no material added from the AFM measurement remained (such as carbon residue) and that any damage during transport or analysis was accounted for before subsequent corrosion. All samples were then returned to the autoclave and testing continued. This process cycled until corrosion time was complete.

On completion, Raman imaging was done on one of each coated sample type, along with XRD as a complementary phase analysis. Raman was used to obtain information on the chemical makeup of the coating surfaces following exposure and XRD was used as a complementary technique. However, significant corrosion product signals were not obtained from XRD after the first few exposures, and thus XRD was discontinued in the later portions of the test matrix and is not reported in this work. Coated samples were then coated in Cu by electrodeposition from a CuSO_4 solution, cut longitudinally and mounted in conductive epoxy such that the interface was visible and polished for EBSD. The Cu coating was performed to minimize delamination of or damage to the coating during the cutting, mounting, and polishing process. SEM imaging was done on the Hitachi S4800 in HTML and the TESCAN MIRA3 in the Low Activation Materials Design and Analysis Laboratory (LAMDA).

Based on a large height variation across the SiC/coating/epoxy interfaces identified by optical microscopy, EBSD strain-mapping was not able to be performed. Stresses across the interfaces were therefore attempted using Transmission Kikuchi Diffraction (TKD) which is a similar technique to EBSD but using the diffracted electron beam transmitted through the foil. However, the grain size of the coating near the interface was too small to facilitate this analysis (<100 nm on the short edge of the grain), as discussed in section 4.5.1.

3.3 MIT Irradiation Campaign

There has been some work indicating that irradiation damage accelerates the aqueous corrosion rates of SiC [91]. Additionally, the chemical aggressiveness of the water is well known to substantially increase via radiolysis. Therefore, several samples were irradiated at the MIT reactor to evaluate the effects of radiation damage, corrosion without radiation damage, corrosion with radiation damage, and corrosion in the presence of gammas (only radiolysis).

A set of two exposures were planned and performed by Caen Ang in consultation with David Carpenter, and other relevant researchers for this and other radiation campaigns. The dry (damage only) test consisted of 66 full days of irradiation to a damage of about 0.5 dpa with a total fluence of 4.8×10^{24} n/m² [115-117]. The temperature varied between about 270-340°C, as indicated by three thermocouples located at different regions of the sample holder. Samples were

held in a block of 6 graphite cylinders sealed together before loading. All samples were separated from the edge and each other by Si spacers and held in place by a Mo spring.

3.3.1 Wet Exposure Test Parameters and Radiolysis Model

Because the MITR is a low temperature reactor, a specialized autoclave system was built to provide LWR-relevant conditions [118]. Water was continuously conditioned to PWR-like chemistry (1200 ppm B, 4.3 ppm LiOH, and corresponding pH of 6.6) through a series of filters, demineralizers, chemical additions and tanks providing gas exchange. In this system, water was pressurized and heated to near 300°C before being pumped into the core at approximately 18 L/min. Samples were positioned at three locations: in core, above-core, and out-of-core. Coolant water flowed through the core, over the in-core samples to the above core section and flowed out of the core into a horizontal autoclave where the out-of-core specimens were housed. This corresponds to a residence time of 1.9 seconds in the core (samples encountered at 1.7 seconds), 4.6 seconds above the core (samples encountered at 3.7 seconds), and about 21 seconds out of the core until reaching the out-of-core samples. The tests were carried out over 127 total active exposure days.

Within the core, specimens were exposed to a flux of damaging neutrons, non-damaging ionizing irradiation and subsequent radiolysis products, providing the most aggressive corrosion environment. Neutron flux in the core is reported in Table 3.6. Using the correlation of 1×10^{21} n/cm² (E > 0.1 MeV) per 1 dpa [21], the samples were estimated to be damaged to about 1 dpa. Above the core, neutron flux was near-zero and the ionizing gamma flux was reduced by an order-of-magnitude, simulating radiolysis without crystalline displacement. Location of a sample set in the loop external to the core eliminated all radiation effects to negligible levels, thus focusing on the PWR-chemistry alone. 4wppm H₂ was added to the coolant to help suppress radiolysis products [119], whose concentrations were calculated using the AECL model [120].

The specific Python code is provided in Appendix C along with the input and output files used to determine radiolysis product concentrations. Table 3.6 gives the neutron flux of three different neutron energy groups at the in-core location for both the CMC and CVD samples. Table 3.7 contains the energy deposition rates from gamma and neutron fluxes calculated in and above the core at the CVD sample locations. Out of the core, the energy deposition was assumed to be zero. Rate constants and included reactions are presented in Table 3.8 the decomposition of water, where the explicit concentration of water is used.

3.3.1 Coating Materials

Four different types of coatings were examined in this work: TiN, CrN, Cr, and multilayered Cr/CrN. All coatings were applied to substrates made from high purity chemical vapor deposited (CVD) SiC, obtained from Rohm and Haas (Deer Park, TX). In addition to the CVD SiC substrate, low resistivity (LR) SiC was obtained from Coorstek (CO, USA) and ceramic matrix composite consisting of Tyranno-SA3 fibers and chemical-vapor infiltrated (CVI) SiC matrix from Hyper-Therm HTC, Inc (CA, USA). All specimens had geometric dimensions near 5x10x1 mm³ with a 2 mm mounting hole. Substrates were coated via the cathodic arc physical vapor deposition (PVD) process by either Techmetals Inc., (OH, USA, referred to as TM) or Richter

Table 3.6: In-core neutron flux of various specimen types. Units are $\text{cm}^{-2}\text{s}^{-1}$ for each entry. Neutron flux is presented in individual component energy fluxes. All CVD SiC samples had the same flux, while the CMC SiC, closer to the core, experienced slightly higher dose.

Specimen Type	$\phi_{n,thermal}$ ($E < 1\text{eV}$)	$\phi_{n,midrange}$ ($1\text{eV} < E < 1\text{MeV}$)	$\phi_{n,fast}$ ($E > 1\text{MeV}$)
CMC SiC	5×10^{13}	1.3×10^{14}	6×10^{13}
CVD SiC	4×10^{13}	9×10^{13}	4×10^{13}

Table 3.7: Energy deposition rates (ED_i) in Gy/s in each location of the MIT water loop, along with G-values (molecules/100 eV) of radiolysis products associated with each type of radiation. Unlisted species have a G-value of 0.

Radiation Type	ED_{Core}	ED_{Above}	$ED_{external}$	G_{H^+, e_{aq}^-}	G_H	G_{OH}	G_{H_2}	$G_{H_2O_2}$	G_{HO_2}
Neutron	110	0.2	0	3.43	1.56	5.74	0.64	0.27	0
Gamma	1300	35.7	0	1.29	0.59	2.87	1.00	0.40	0.03

Table 3.8: Reactions and associated rate constants used for radiolysis modeling. The concentration of water is not a factor of the rate, except in the decomposition reaction (#23). Rate constants are in units of $\text{M}^{-1}\text{s}^{-1}$ or s^{-1} , as relevant.

<i>Reaction number</i>	<i>Rate Constant</i>	<i>Reaction</i>	<i>Reaction number</i>	<i>Rate Constant</i>	<i>Reaction</i>
1	5.95×10^6	$2 \text{ H}_2\text{O} + 2 \text{ e}^- \rightarrow 2 \text{ OH}^- + \text{H}_2$	22	1.13×10^{12}	$\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$
2	1.04×10^{11}	$2 \text{ H} \rightarrow \text{H}_2$	23	6.52×10^{-2}	$\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$
3	9.86×10^9	$2 \text{ OH} \rightarrow \text{H}_2\text{O}_2$	24	5.69×10^{11}	$\text{H}^+ + \text{HO}_2^- \rightarrow \text{H}_2\text{O}_2$
4	4.96×10^{11}	$\text{H}_2\text{O} + \text{e}^- + \text{H} \rightarrow \text{OH}^- + \text{H}_2$	25	25.2	$\text{H}_2\text{O}_2 \rightarrow \text{H}^+ + \text{HO}_2^-$
5	3.72×10^{11}	$\text{e}^- + \text{OH} \rightarrow \text{OH}^-$	26	1.76×10^8	$\text{H}_2\text{O} + \text{HO}_2^- \rightarrow \text{OH}^- + \text{H}_2\text{O}_2$
6	6.34×10^{10}	$\text{H} + \text{OH} \rightarrow \text{H}_2\text{O}$	27	1.36×10^{11}	$\text{OH}^- + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2^-$
7	2.85×10^{11}	$\text{e}^- + \text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{OH}^-$	28	5.69×10^{11}	$\text{H}^+ + \text{O}^- \rightarrow \text{OH}$
8	2.18×10^{11}	$\text{e}^- + \text{O}_2 \rightarrow \text{O}_2^-$	29	25.2	$\text{OH} \rightarrow \text{H}^+ + \text{O}^-$
9	1.61×10^{11}	$2 \text{ H}_2\text{O} + \text{e}^- + \text{O}_2^- \rightarrow 2 \text{ OH}^- + \text{H}_2\text{O}_2$	30	1.76×10^8	$\text{H}_2\text{O} + \text{O}^- \rightarrow \text{OH} + \text{OH}^-$
10	1.61×10^{11}	$\text{e}^- + \text{HO}_2 \rightarrow \text{HO}_2^-$	31	1.36×10^{11}	$\text{OH} + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{O}^-$
11	2.14×10^9	$\text{H} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{OH}$	32	5.69×10^{11}	$\text{H}^+ + \text{O}_2^- \rightarrow \text{HO}_2$
12	6.06×10^{10}	$\text{H} + \text{O}_2 \rightarrow \text{HO}_2$	33	1.55×10^5	$\text{HO}_2 \rightarrow \text{H}^+ + \text{O}_2^-$
13	2.13×10^{11}	$\text{H} + \text{HO}_2 \rightarrow 2 \text{ OH}$	34	2.87×10^4	$\text{H}_2\text{O} + \text{O}_2^- \rightarrow \text{OH}^- + \text{HO}_2$
14	2.13×10^{11}	$\text{H} + \text{O}_2^- \rightarrow \text{HO}_2^-$	35	1.36×10^{11}	$\text{OH}^- + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2^-$
15	4.23×10^8	$\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$	36	7.16×10^{11}	$\text{e}^- + \text{H}^+ \rightarrow \text{H}$
16	8.97×10^{10}	$\text{OH} + \text{O}_2^- \rightarrow \text{OH}^- + \text{O}_2$	37	1.65×10^5	$\text{H} \rightarrow \text{e}^- + \text{H}^+$
17	3.2×10^{10}	$\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$	38	2.01×10^3	$\text{H}_2\text{O} + \text{e}^- \rightarrow \text{H} + \text{OH}^-$
18	4.1×10^7	$2 \text{ HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	39	8.01×10^9	$\text{H} + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{e}^-$
19	4.81×10^8	$\text{H}_2\text{O} + \text{HO}_2 + \text{O}_2^- \rightarrow \text{OH}^- + \text{H}_2\text{O}_2 + \text{O}_2$	40	7.8×10^8	$\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$
20	3.5×10^7	$2 \text{ H}_2\text{O} + 2 \text{ O}_2^- \rightarrow 2 \text{ OH}^- + \text{H}_2\text{O}_2 + \text{O}_2$	41	2.1×10^3	$\text{H}_2\text{O} + \text{H} \rightarrow \text{OH} + \text{H}_2$
21	3.78×10^{-2}	$\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + 0.5 \text{ O}_2$	42	8.18×10^{10}	$\text{OH} + \text{HO}_2^- \rightarrow \text{H}_2\text{O} + \text{O}_2^-$

Table 3.8 Continued

<i>Reaction number</i>	<i>Rate Constant</i>	<i>Reaction</i>	<i>Reaction number</i>	<i>Rate Constant</i>	<i>Reaction</i>
44	8.76×10^{10}	$\text{HO}_2^- + \text{O}^- \rightarrow \text{OH}^- + \text{O}_2^-$	47	3.26×10^{10}	$\text{O}^- + \text{O}_2 \rightarrow \text{O}_3^-$
45	1.55×10^9	$\text{H}_2 + \text{O}^- \rightarrow \text{H} + \text{OH}^-$			

Precision, Inc., (PA, USA, referred to as RP). The CrN samples from Techmetals included a Ti compatibility layer (~10nm) and certain other samples were reported to be pre-coated with electroless Ni at ORNL. Details of the coating process are described elsewhere [112, 121]. Exact details of the coating process are not known as the coatings are proprietary. Coating stoichiometry is reported in Table 3.4 (the same analysis as in the previous section). Details of exposure conditions for each sample in the Ar condition are given in Table 3.9.

3.3.2 Sample Examination

Samples irradiated in Ar at the MITR were transported to ORNL where they were examined by optical microscopy on a Keyence VHX-1000 digital microscope followed by X-ray diffraction (XRD) using a Bruker D2 Phaser, 2nd Generation instrument with a Si standard for displacement correction. The program GSAS-II was used to perform Rietveld refinement [122] for lattice parameter (and thus lattice swelling) determination. Following these procedures, samples were mounted in epoxy, cross-sectioned, and polished. Focused ion beam (FIB) was used to obtain liftouts for Transmission Electron Microscopy (TEM), which was conducted on LAMDA's FEI Talos F200X S/TEM and JEOL2100F TEM instruments. SEM was performed with the TESCAN MIRA3 on the cross-sections to observe cracking behavior.

Prior to testing, the samples selected for MITR water exposure were weighed at ORNL and again at MIT with a precision of 0.01 mg, where dimensions were obtained using calipers with a precision of 0.01 mm. Following exposure, samples were transported to ORNL where they were cleaned in acetone and weighed a minimum of three times to obtain a precise mass measurement. Each sample was then examined with the Keyence, XRD, SEM, and TEM as above with the samples irradiated in Ar.

3.3.3 Coating Stresses

The $\sin^2(\psi)$ X-ray diffraction method was used by Peter Mouche to measure the residual stress in the coatings, presented in Table 3.10. Measurements were made on a Scintag PTS goniometer with a Cr K_α ($\lambda=2.28970\text{\AA}$) source, a liquid nitrogen cooled Ge detector, and a radial divergence limiting parallel plate collimator. Nine sets of spectra were collected from $\psi=-55^\circ$ to $+55^\circ$ on the highest angle peaks that gave reasonable intensity. To calculate the residual stresses, the following Young's Moduli for Cr, CrN, and TiN were obtained from literature: $E_{\text{Cr}} = 280 \text{ GPa}$ [123], $E_{\text{CrN}} = 250 \text{ GPa}$ [123, 124] and $E_{\text{TiN}} = 250 \text{ GPa}$ [125, 126]. A Poisson ratio of $\nu = 0.2$ was used for the Cr and CrN coatings while 0.28 was used for TiN. The lattice parameter for the peak from the ψ_0 position was used for the unstrained value d_0 . Minimal splitting of the positive and negative ψ values occurred, so both were fit when calculating the stress using equation 3.1:

$$\sigma = \frac{E}{1 + \nu} \frac{1}{d_0} \left(\frac{\partial d_\psi}{\partial \sin^2 \psi} \right) \quad \text{Eqn.3.1}$$

For purposes of coating stress estimations in the discussion, the coefficients of thermal expansion (CTE) for each material were assigned by the relationship given by Snead et al [21] for SiC ($4.7 \times 10^{-6}/\text{K}$ at 300°C), by Saringer et al. [126] for TiN ($8.9 \times 10^{-6}/\text{K}$ at 300°C), and by fitting the data in Zhou et al [127] for CrN ($6.5 \times 10^{-6}/\text{K}$ at 300°C). The CTE of Cr was assumed to be constant at $4.9 \times 10^{-6}/\text{K}$ [128]. For this work, the coatings were not pure stoichiometric materials,

Table 3.9: Samples exposed to neutron irradiation with Ar cover gas. Total neutron fluence $4.8 \times 10^{24} \text{ n/m}^2$ ($>0.1 \text{ MeV}$). CVD denotes high purity, high resistivity CVD SiC, LRCVD denotes high purity low resistivity SiC, and CMC denotes a CMC plate specimen.

Sample Designation	Coating	Type of SiC Substrate	Coating Thickness (μm)	Irradiation Temperature ($^{\circ}\text{C}$)	Compatibility Layer
<i>TiN-CVD</i>	TiN	High Resistivity CVD	3	340	-
<i>TiN-LRCVD</i>		Low Resistivity CVD	3	320	-
<i>TiN-CMC</i>		CMC	3	330	-
<i>CrN-CVD</i>	CrN	High Resistivity CVD	3	320	Ti
<i>CrN-LRCVD</i>		Low Resistivity CVD	4	330	Ti
<i>CrN-cp-CVD</i>		High Resistivity CVD	3	305	Ti/Ni
<i>CrN-CMC</i>		CMC	4	340	Ti/Ni
<i>Cr-CVD</i>	Cr	High Resistivity CVD	18	330	-
<i>Cr-CMC</i>		CMC	18	340	-
<i>Cr-cp-CMC</i>		CMC	17	320	Ni
<i>CrN-ml</i>	Cr/CrN multilayer	High Resistivity CVD	18	290	Ni
<i>CrN-ml2</i>		High Resistivity CVD	16	330	Ni

Table 3.10: Residual stresses in as-received coatings deposited on CVD SiC (from R&H) as determined by XRD. Positive stresses are tensile.

Coating	Residual Stress (GPa)
<i>Cr</i>	0.22 ± 0.014
<i>Cr/CrN multilayer</i>	-0.60 ± 0.12
<i>CrN</i>	-1.28 ± 0.13
<i>TiN</i>	-1.66 ± 0.22

so the specific CTEs may be somewhat different than published values.

3.3.4 Uncoated SiC Materials

The uncoated SiC materials were only included in the three wet exposures since SiC's radiation properties have been well studied. Five different material types were included in each of the three loop locations and are presented in Table 3.11. Three SiC variants had a highly faulted polycrystalline cubic structure and were manufactured by CVD. Rohm and Haas (R&H) produced one high electrical resistivity, high purity variant (HR). The other two were HR variant from Coorstek from two different sample batches (labeled HR and HR2). Each of these had grain diameters on the order of 5 μm with less than 5ppm total impurities and <1ppm N. Comparison of the high resistivity samples allows the effect of any manufacturing differences to be quantified. Samples from both vendors are well-studied in literature [11, 107, 129, 130]. In addition, single crystal 6H SiC with a (0001) surface was sourced from MTI corporation for evaluation of grain boundary corrosion effects by comparison to the CVD samples. These samples were doped with N to achieve resistivities between 0.02 and 0.2 $\Omega\text{-cm}$. The scoping tests performed at GE (sections 3.1.2, 4.1.3, and 6.2.2) has demonstrated that 6H SiC corrodes similarly to cubic SiC in the absence of significant grain boundary attack. Finally, the CMC SiC tubes were manufactured by General Atomics using Hi-Nicalon-S fibers and a 150 nm PyC interphase layer. Matrix SiC was infiltrated into the fiber preform by CVI and then applied as a top-coat by CVD to a thickness of up to 40 μm . Each CMC sample was then cut from a larger rod with roughly 40% fiber-volume fraction and 15% porosity, exposing the fibers on cut ends. In each test condition one of each CMC and 6H SiC sample was exposed along with two of each CVD variant.

Prior to the tests, each sample was weighed at ORNL (with a precision of 0.01 mg), transported to MIT, re-weighed and the dimensions were measured with calipers (with a precision of 0.01 mm) prior to insertion. Following the tests, samples were photographed and transported to ORNL where they were cleaned with acetone and weighed. For the CMC samples, given the possibility of monolith cracking leading to water retention in the CMC matrix, the samples were heated for 15 minutes and again for 45 minutes between 110 and 120°C in air to bakeout any retained water [131]. They were then reweighed as previously described. The surfaces of certain CVD SiC samples were examined by Scanning Electron Microscopy (SEM) on a TESCAN MIRA3 instrument in ORNL's Low Activation Materials Development and Analysis (LAMDA) laboratory. Select samples were then mounted in epoxy, cross-sectioned, and polished for additional SEM evaluation.

A summary of materials discussed in this chapter is presented in Table 3.12.

Table 3.11: SiC sample types included in the MITR.

<i>Sample Type</i>	<i>Manufacturer</i>	<i>Description</i>
<i>CMC SiC</i>	General Atomics	Hi-Nicalon S Fibers with CVI Matrix
<i>6H SiC</i>	MTI Corporation	Single crystal monolith, presenting (0001) surface
<i>R&H HR</i>	Rohm & Haas	Polycrystalline, high resistivity, monolithic
<i>Coorstek HR</i>	Coorstek	Polycrystalline, high resistivity, monolithic
<i>Coorstek HR2</i>	Coorstek	Polycrystalline, high resistivity, monolithic

Table 3.12: Summary of specimens used in this study. HHT and HR are high resistivity, LR is low resistivity. Specifics of each condition are given in Table 3.1, Table 3.2, and Table 3.3 on page 45. For samples at MIT, prefix characters indicate if corrosion, “C”, radiolysis, “R”, or radiation damage, “I”, are present. Other designations show coating vendors and material type.

<i>Specimen Designation</i>	<i>Material Type</i>	<i>Vendor</i>	<i>Coating type</i>	<i>Coating Vendor</i>	<i>Corrosion Environment or Comment/Reference Section</i>	<i>Corrosion time/Increment or Irradiation Temperature</i>	<i>Lab</i>
<i>SiC-HR</i>	CVD SiC-HR	Coorstek	N/A	N/A	PWR BWR-HWC BWR-NWC/ Section 3.1	3 months/ 1 month	General Electric
<i>SiC-LR</i>	CVD SiC-LR	Coorstek					
<i>SiC-4H</i>	CVD SiC-4H	University Wafer (UW)					
<i>SiC-HHT</i>	CVD SiC-HR	R&H					
<i>SiO₂</i>	SiO ₂	UW					
<i>Si</i>	Si	UW					
<i>Poly-Al₂O₃</i>	Polycrystalline Al ₂ O ₃	Coorstek					
<i>Al₂O₃</i>	Single crystal Al ₂ O ₃	Coorstek					
<i>DB-ZrN</i>	CVD SiC	R&H	ZrN	DB	BWR-NWC BWR-HWC/ Section 3.1	NWC- 400h/ 200h HWC-400h/ 200,50,150 h	ORNL Hydrothermal Corrosion Lab
<i>TM-TiN</i>	CVD SiC	R&H	TiN	TM			
<i>RP-Cr</i>	CVD SiC	R&H	Cr	RP			
<i>ORNL NiCr</i>	CVD SiC	R&H	NiCr	ORNL			
<i>RP-CrN</i>	CVD SiC	R&H	CrN	RP			
<i>ORNL Ni</i>	CVD SiC	R&H	Ni	ORNL			
<i>TiN</i>	TiN-1wt%Ni	Coorstek	N/A	N/A			
<i>Cr</i>	Japenese Cr	ORNL					
<i>NGNP CMC</i>	CMC SiC/ Nicalon-S Fibers	Tyranno (fibers) Hypertherm (CVI)					
<i>SiC</i>	CMC SiC/ SA3 Fibers						
<i>Hypertherm CMC SiC</i>	CMC SiC/ SA3 Fibers						

Table 3.12 Continued

<i>Specimen Designation</i>	Material Type	Vendor	Coating type	Coating Vendor	Corrosion Environment or Comment/ Reference Section	Corrosion time/ Increment or Irradiation Temperature	Lab
<i>R&H SiC</i>	CVD SiC	R&H					
<i>up-SiC</i>	Unpolished SiC	R&H	N/A	N/A	HWC NWC PWR 320°C 3ppm H ₂ 320°C 2ppm O ₂ 350°C 4ppm O ₂ 350°C 2ppm O ₂ 350°C 1ppm O ₂ / Section 3.2	LWR: 2000-2600h/ 200-500h Others: 400-600h/ 200h	ORNL Hydrothermal Corrosion Lab
<i>p-SiC</i>	Polished SiC	R&H				LWR: 2000/500h Others: 400-600h/ 50-200h	
<i>TM-CrN</i>	CVD SiC	R&H	CrN	TM	HWC NWC PWR 320°C 3ppm H ₂ 350°C 4ppm O ₂ 350°C 2ppm O ₂ 350°C 1ppm O ₂ / Section 3.2	LWR: 2000-2600h/ 200-500h	
<i>RP-CrN</i>	CVD SiC	R&H	CrN	RP			
<i>TM-TiN</i>	CVD SiC	R&H	TiN	TM		Others: 400-600h/ 200h	
<i>RP-Cr</i>	CVD SiC	R&H	Cr	RP			
<i>I-TM-CrN</i>	CVD-SiC	R&H	CrN	TM	No corrosion, only irradiation to	320°C	
<i>I-TM-Ni/CrN</i>	CVD-SiC	R&H	Ni/CrN	TM		305°C	

Table 3.12 Continued

Specimen Designation	Material Type	Vendor	Coating type	Coating Vendor	Corrosion Environment or Comment/ Reference Section	Corrosion time/ Increment or Irradiation Temperature	Lab
<i>I-RP-Ni/Cr/CrN</i>	CVD SiC	R&H	Ni/Cr/CrN/Cr/CrN	RP	0.5 dpa and 4.8×10^{24} n/m ² over 66 days /	290°C, 330°C	MIT: Irradiation without corrosion ORNL: Analysis in LAMBDA
<i>I-RP-Cr</i>	CVD SiC	R&H	Cr	RP	Section 3.3	330°C, 340°C	
<i>I-TM-TiN</i>	CVD SiC	R&H	TiN	TM		340°C	
<i>I-RP-L-Cr</i>	CVD SiC LR	Coorstek	Cr	RP	No corrosion, only irradiation/	330°C	
<i>I-RP-L - Ni/Cr/CrN</i>	CVD SiC LR	Coorstek	Ni/Cr/CrN	RP		330°C	
<i>I-TM-L-CrN</i>	CVD SiC LR	Coorstek	CrN	TM		330°C	
<i>I-TM-L-TiN</i>	CVD SiC LR	Coorstek	TiN	TM		320°C	
<i>I-RP-CMC-CrN</i>	CMC SiC/ SA3 fibers	Tyranno (fibers) Hypertherm (CVI)	Cr/CrN/Cr/CrN	RP		270°C, 340°C	
<i>I-RP-CMC-Ni/CrN</i>	CMC SiC/ SA3 fibers	Tyranno (fibers) Hypertherm (CVI)	Ni/Cr/CrN/Cr/CrN	RP		270°C, 340°C	
<i>I-TM-CMC-CrN</i>	CMC SiC/ SA3 fibers	Tyranno (fibers) Hypertherm (CVI)	CrN	TM		340°C	
<i>I-RP-CMC-Cr</i>	CMC SiC/ SA3 fibers	Tyranno (fibers) Hypertherm (CVI)	Cr	RP		320°C, 340°C	
<i>I-RP-CMC-Ni/Cr</i>	CMC SiC/ SA3 fibers	Tyranno (fibers) Hypertherm (CVI)	Ni/Cr	RP		320°C	
<i>I-TM-CMC-TiN</i>	CMC SiC/ SA3 fibers	Tyranno (fibers)	TiN	TM		330°C	

Table 3.12 Continued

<i>Specimen Designation</i>	<i>Material Type</i>	<i>Vendor</i>	<i>Coating type</i>	<i>Coating Vendor</i>	<i>Corrosion Environment or Comment/ Reference Section</i>	<i>Corrosion time/ Increment or Irradiation Temperature</i>	<i>Lab</i>
<i>C-RP-CrN</i> <i>C-RP-Cr</i> <i>C-TM-TiN</i> <i>C-RP-CMC-Cr</i> <i>C-SiC-HHT</i> <i>C-SiC-HR</i> <i>C-SiC-HR2</i> <i>RC-RP-CrN</i> <i>RC-RP-Cr</i> <i>RC-TM-TiN</i> <i>RC-RP-CMC-Cr</i> <i>RC-SiC-HHT</i> <i>RC-SiC-HR</i> <i>RC-SiC-HR2</i> <i>IRC-RP-CrN</i> <i>IRC-RP-Cr</i> <i>IRC-TM-TiN</i> <i>IRC-RP-CMC-Cr</i> <i>IRC-SiC-HHT</i>		Hypertherm (CVI)					
	CVD SiC	R&H	CrN	RP	Out of core corrosion (no irradiation or radiolysis)	300°C	MIT: Corrosion ORNL: Analysis in LAMBDA
	CVD SiC	R&H	Cr	RP			
	CVD SiC	R&H	TiN	TM			
	CMC SiC	Tyranno (fibers),Hypertherm (CVI)	Cr	RP			
	CVD SiC HHT	R&H	N/A	N/A			
	CVD SiC HR	Coorstek					
	CVD SiC HR	Coorstek					
	CVD SiC	R&H	CrN	RP	Above core corrosion without radiation damage; only radiolysis	300°C	
	CVD SiC	R&H	Cr	RP			
	CVD SiC	R&H	TiN	TM			
	CMC SiC	Tyranno (fibers),Hypertherm (CVI)	Cr	RP			
	CVD SiC HHT	R&H	N/A	N/A			
	CVD SiC HR	Coorstek					
	CVD SiC HR	Coorstek					
CVD SiC	R&H	CrN	RP	In core corrosion with radiation damage	300°C	MIT: Corrosion	
CVD SiC	R&H	Cr	RP				
CVD SiC	R&H	TiN	TM				
CMC SiC	Tyranno (fibers),Hypertherm (CVI)	Cr	RP				
CVD SiC HHT	R&H	N/A	N/A				

Table 3.12 Continued

<i>Specimen Designation</i>	Material Type	Vendor	Coating type	Coating Vendor	Corrosion Environment or Comment/ Reference Section	Corrosion time/ Increment or Irradiation Temperature	Lab
<i>IRC-SiC-HR</i>	CVD SiC HR	Coorstek					ORNL: Analysis in LAMBDA
<i>IRC-SiC-HR2</i>	CVD SiC HR	Coorstek					

Chapter 4: Experimental Results

4.1 Scoping Tests

As described in chapter 3, the scoping studies were intended to obtain a preliminary analysis of the corrosion characteristics of SiC, specifically determining the qualitative viability of corrosion mitigation coatings on SiC along with obtaining differences in rate relationships of different variants of SiC and its common impurities in non-CVD processes.

4.1.1 GE Uncoated Materials Corrosion

All SiO₂ samples dissolved completely within the first month and only one Si sample survived the first month. The remaining sample, which was exposed to BWR-NWC conditions had lost 33% of its initial weight. It completely dissolved in the second month. The exposure results of Al₂O₃ and SiC are given in separate sections below.

4.1.2 Alumina Corrosion Characteristics

Mass loss is shown in Figure 4.1 for polycrystalline (b) and single crystal (b) samples in all three conditions. From Figure 4.1, single crystal dissolution is slower than for the polycrystalline materials with recession rates highest in BWR-HWC, slower in PWR, and slowest in BWR-NWC. Surface microscopy of the alumina samples is presented in Figure 4.2 and Figure 4.3. Figure 4.2 compares SEM micrographs for single crystal samples from each condition. The images are indistinguishable with no indication of localized corrosion. Figure 4.3 shows low magnification images of polycrystalline alumina exposed to each of the three water chemistries. These are also indistinguishable, and each sample shows clearly protruding regions of alumina that appear to be individual grains.

Subsequent Raman spectra are given in Figure 4.4 with corresponding peak identifications. Several Al₂O₃ (corundum) peaks were present in the polycrystalline case, Figure 4.4a, but were not seen in the single crystal spectrum, Figure 4.4b. Fundamental α -Al₂O₃ peaks from the single crystal case are at 417, 450, 576, and 750 cm⁻¹. The polycrystalline spectra add in additional α -Al₂O₃ peaks at 645 and 378 cm⁻¹. These peaks are also seen in reference [74] and seem to be unique to the polycrystalline case.

A few additional peaks, only present in the NWC-exposed sample, are observed in Figure 4.4a and represent diascore, AlO(OH), having peaks near 287, 330, 447, 498, 792 cm⁻¹ (see [132-134] for comparison of aluminum oxide/hydroxide mineral spectra). No choice of locations on the sample showed diascore peaks in HWC or PWR samples and different locations on NWC samples gave varying spectra. Some results showed only corundum peaks, while others showed almost only diascore peaks, with the rest having mixtures of the two. The presented spectrum for the NWC polycrystalline case is representative of a mixed-species spectrum.

4.1.3 SiC Corrosion Characteristics

Figure 4.5a-c shows the mass losses for NWC, PWR, and HWC, respectively. Generally, mass losses were such that NWC > PWR > HWC. Except for the LR sample exposed to NWC, and the HR sample exposed to PWR, there is little difference among specimen types.

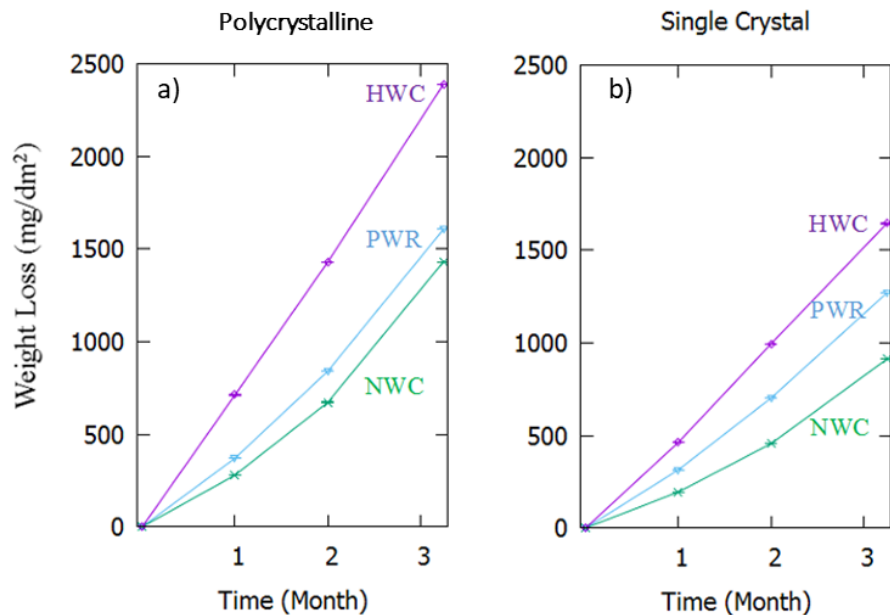


Figure 4.1: Alumina mass loss data for both a) polycrystalline and b) single crystalline microstructures over 3 months in PWR, BWR-HWC, and BWR-NWC chemistry conditions. The chemistry conditions are labeled on the graphs.

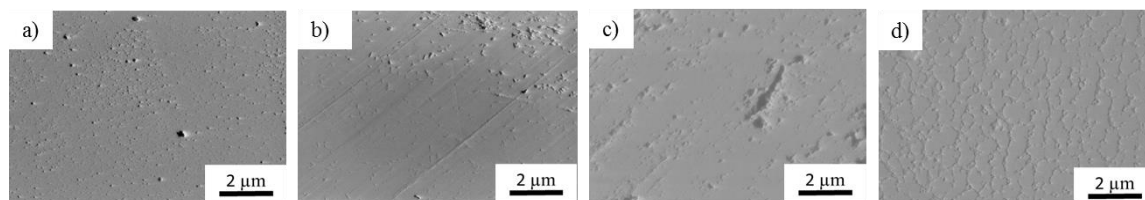


Figure 4.2: SEM-SE (secondary electron) photographs of single crystal alumina. a) is a reference sample that was un-corroded and after exposure for 3 months in b) PWR, c) BWR-HWC, and d) BWR-NWC.

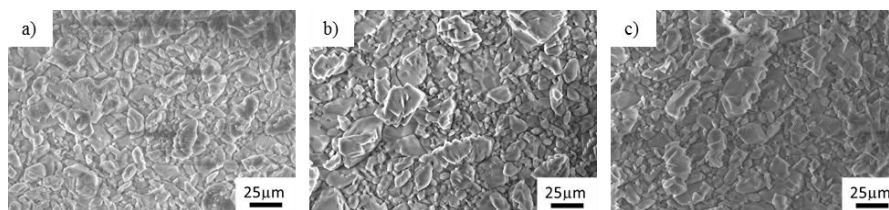


Figure 4.3: SEM-SE images of polycrystalline alumina corroded under a) BWR-HWC b) PWR c) BWR-NWC at low (x1.00k) magnification.

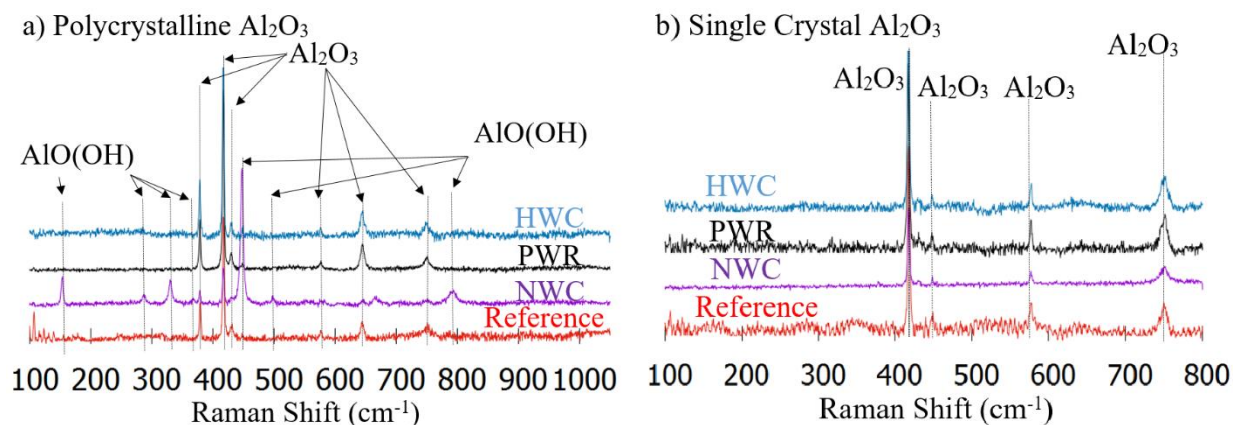


Figure 4.4: Raman spectra of alumina in reference and corroded states. The first graph compares each corroded specimen to the reference for the polycrystalline crystal case. The second graph gives the same comparison for the single crystal case. Peak designations for diasporite ($\text{AlO}(\text{OH})$) and corundum (Al_2O_3) can be found in [132, 135].

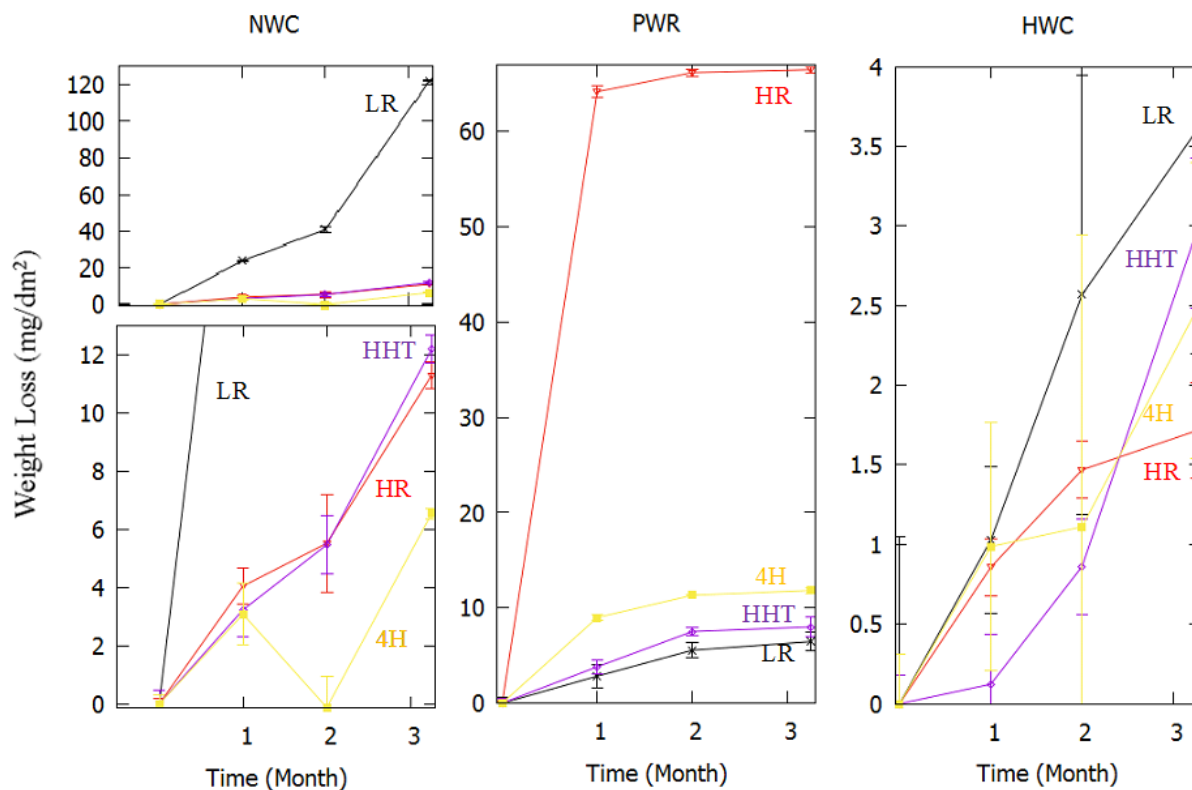


Figure 4.5: Mass loss data for all four SiC variants over time in NWC, PWR, and HWC conditions, respectively, moving from left to right. The lower graph under “NWC” expands the upper graph to show the other three variant trends. Note that each graph has a different scale as labeled above

Under NWC conditions, the LR (low resistivity) SiC sample corroded more quickly than the other variants and was clearly super-linear ($\Delta m/SA \approx 21t^{1.34}$). In the HWC condition, the rate was significantly smaller ($\Delta m/SA \approx 1.2t$) and the sample mass change was indistinguishable within the error, which was relatively large as a consequence of the low mass change. It is significant that the HR and HHT specimens corroded at virtually the same rate and also appeared to be slightly super-linear for NWC-exposed specimens ($\Delta m/SA \approx 3t^{1.1}$), while being closer to linear or parabolic for the HWC-exposed specimens with dramatically less mass loss. The 4H-SiC samples exposed to NWC conditions corroded at similar rate to the high resistivity samples from 0 to 1 month and from 2 to 3 months with an increase in mass to a net 0 change between months 1 and 2. In PWR water, all variants corroded parabolically. The HR variant had the largest total mass loss, but after the large mass loss following 1 month, it corroded at a similar rate to the others. In absolute mass loss $HR > 4H > HHT > LR$.

Microscopy of LR SiC is presented in Figure 4.6 for each of the three chemistries and the starting morphology. In Figure 4.6d and Figure 4.6h significant grain-fallout was observed for NWC-exposed samples where several grain surfaces appear to be corroding uniformly, while large valleys are created between them. The PWR and HWC micrographs show potential roughening, but no apparent grain boundary attack.

Microscopy of the HR variant, Figure 4.8, shows a greater discrepancy where the reference is most similar to the samples from the HWC condition while the PWR-exposed specimen reveals mostly uniform corrosion with potential roughening. The NWC condition shows the most extensive grain attack/removal. Figure 4.9 provides the best evidence for grain boundary attack, showing regions where grain boundaries are clearly selectively attacked. Such attack was not observed in samples from the PWR or HWC conditions. The HHT variant was similar.

Raman spectra for each of the variants across all chemistries are compared to their references in Figure 4.10. Only SiC is found on the surface of the samples, indicating immediate dissolution of SiO_2 when it forms. In Figure 4.10d for the NWC case, the unmarked peaks do not align with any Si, SiO_2 , or SiC peaks and may be from metal oxide contaminants that deposited on the surface of the specimen.

4.1.4 ORNL HCL Coatings Scoping tests

As described in chapter 3, BWR-HWC and BWR-NWC conditions were simulated with the same coated and monolithic SiC materials, along with some Cr-coated and uncoated CMC SiC. The mass loss results are shown in Figure 4.11-Figure 4.13. Figure 4.11a clearly shows loss of the entire ZrN coating and loss of significant portions of the NiCr coating in the first exposure. Figure 4.11b shows the smaller mass change portion of Figure 4.11a highlighted in a red-dashed box. Ni, TiN, and Cr coatings on CVD SiC either gained or did not lose any mass, while CrN and Cr on CMC SiC lost some mass. Similar behavior was observed in Figure 4.12 for the monolithic samples. The CVD SiC samples further corroded far more slowly than the CMC samples, which had been cut following an outer monolith and thus had exposed fibers. Figure 4.13 shows the coated (a) and monolithic (b) samples from the BWR-NWC environment. Except for Cr, which lost mass, the samples behaved similarly to the HWC condition with significantly

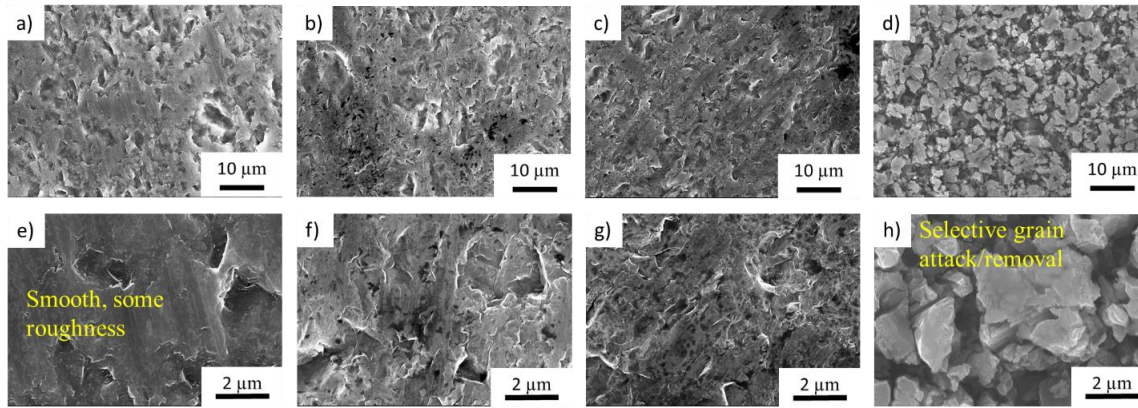


Figure 4.6: SEM micrographs of samples belonging to the SiC-LR variant. Low magnification images are shown in a)-d), and high magnification in e)-h). Figures a) and e), b) and f), c) and g), and d) and h) correspond to the reference sample, and the samples exposed to PWR, HWC, and NWC conditions, respectively. The labels on each row/column reflect this designation.

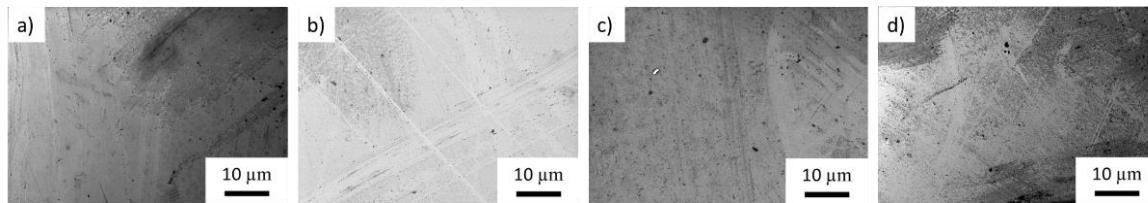


Figure 4.7: SEM-SE micrographs of samples belonging to the SiC-4H variant. a) is the reference sample with b), c), and d) corresponding to PWR, HWC, and NWC exposed samples. The labels on each row/column reflect this designation.

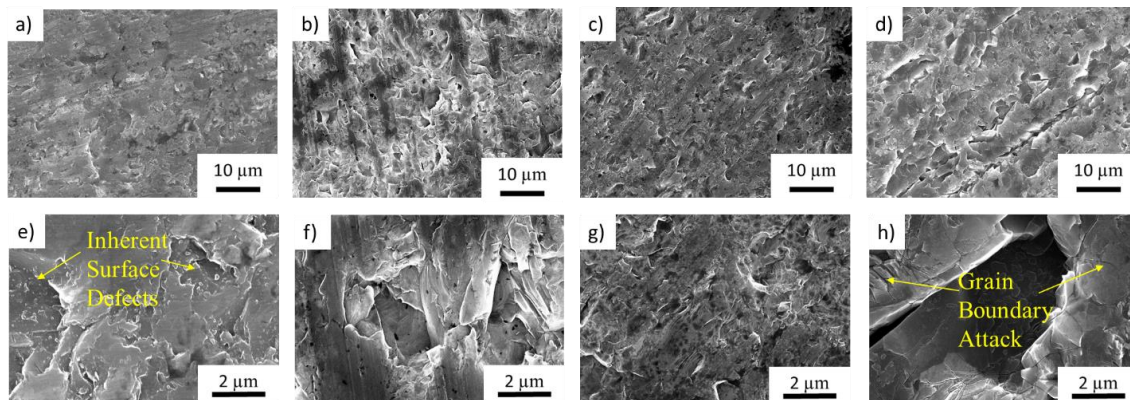


Figure 4.8: SEM-SE micrographs of samples belonging to the SiC-HR variant. Low magnification images are shown in a)-d), and high magnification in e)-h). Figures a) and e), b) and f), c) and g), and d) and h) correspond to the reference sample, and the samples exposed to PWR, HWC, and NWC conditions, respectively. The labels on each row/column reflect this designation.

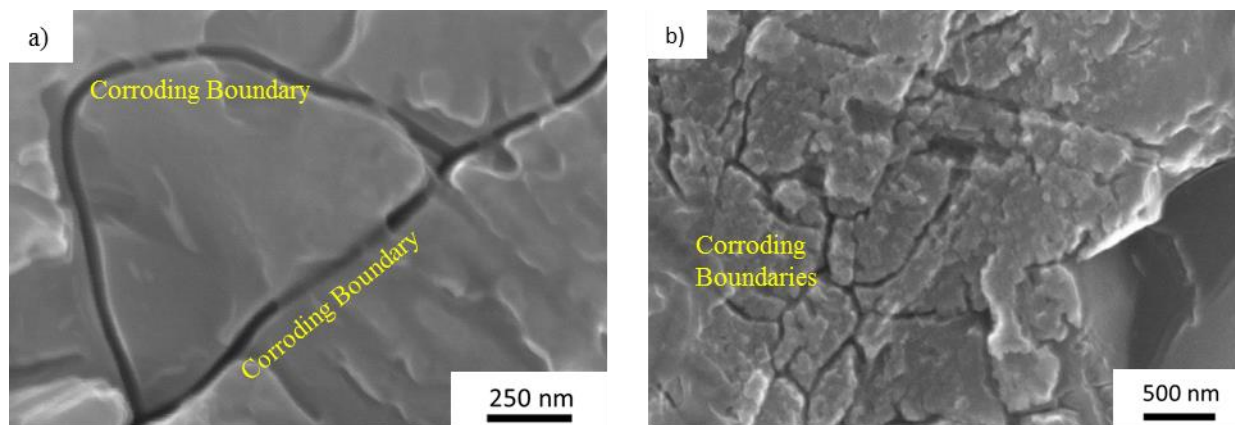


Figure 4.9: High magnification SEM-SE images of a) HR-NWC and b) HHT-NWC revealing grain boundary attack.

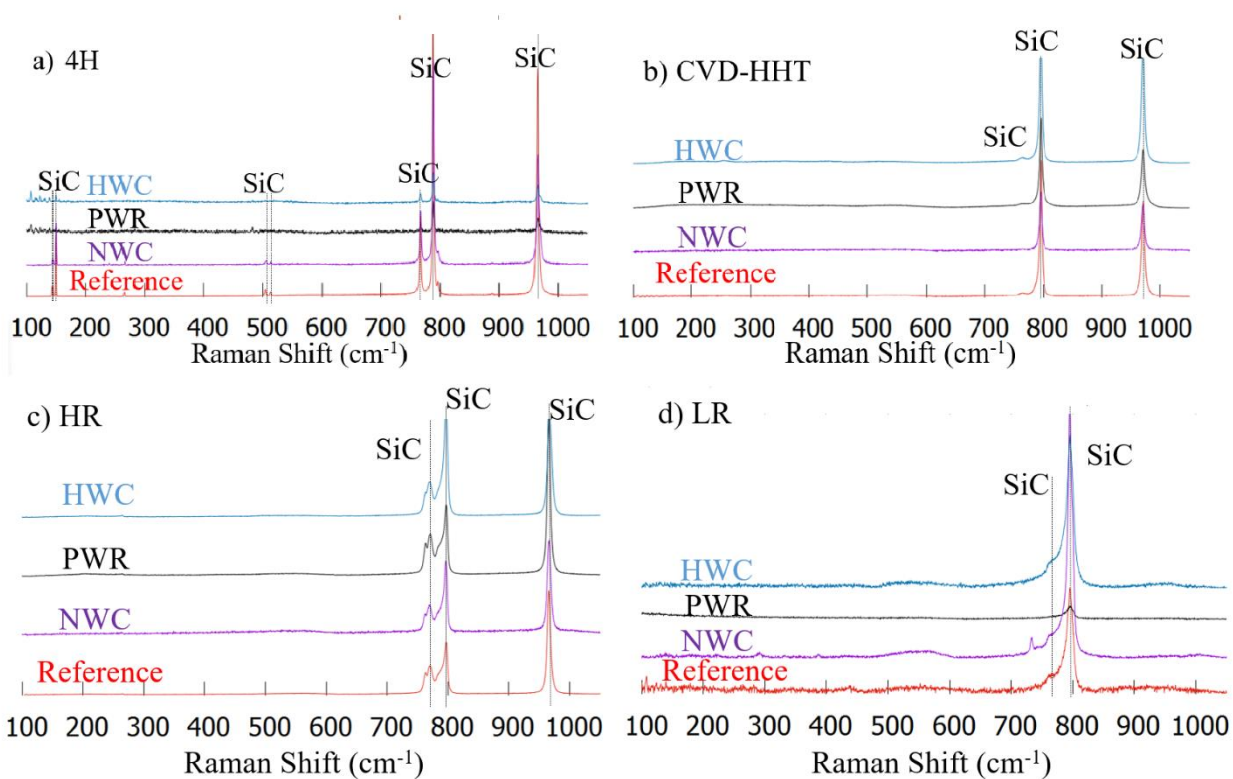


Figure 4.10: Comparison of the Raman spectra for each SiC variant. Sample types are compared to their reference for a) 4H, b) Rohm and Hass (HHT), c) HR, and d) LR.

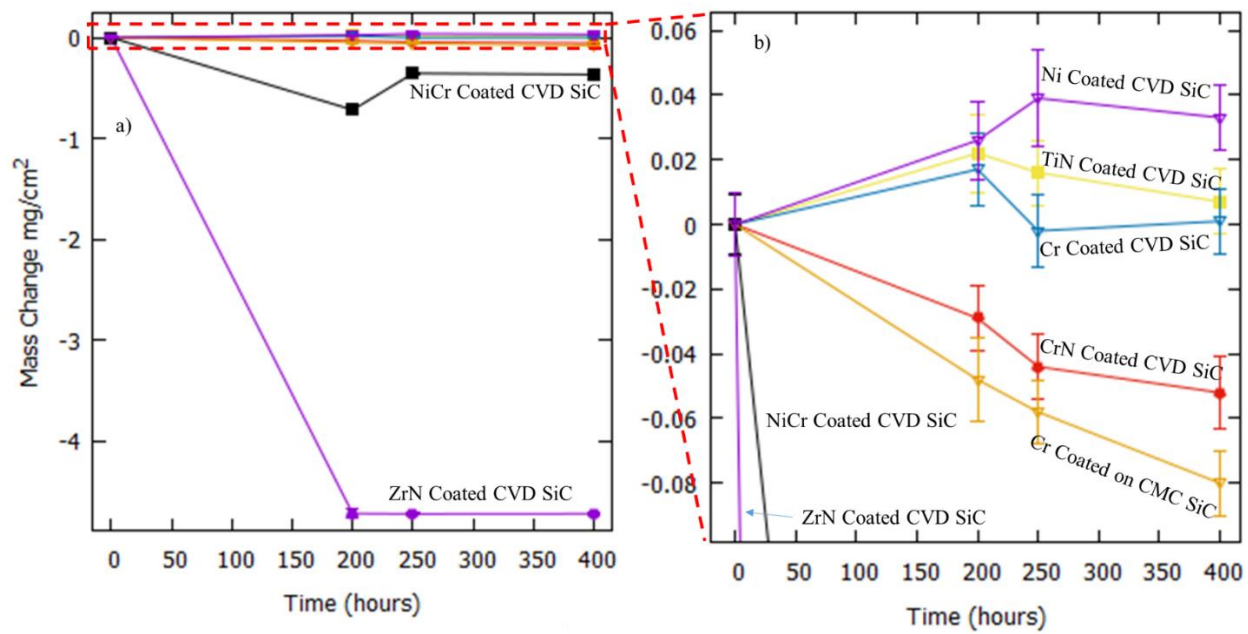


Figure 4.11: Mass change of coated SiC specimens exposed to BWR-HWC conditions for 400h. a) Full-scale figure. b) Zoomed region of samples with small mass change.

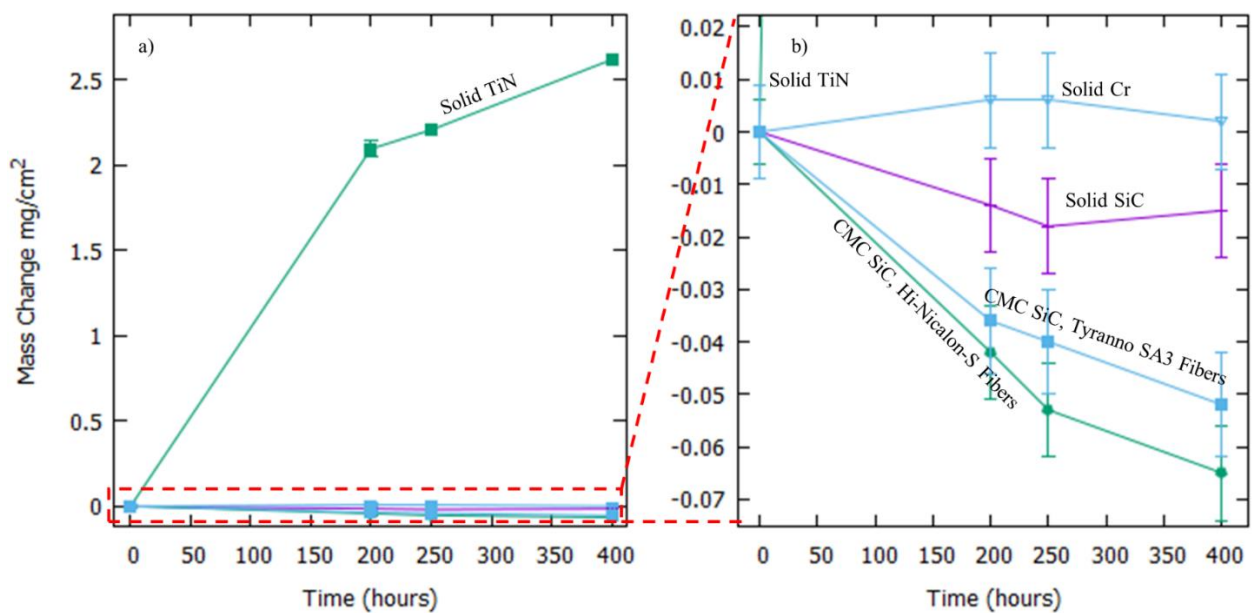


Figure 4.12: Mass change of uncoated SiC and monolithic coating materials exposed to BWR-HWC conditions for 400h. a) Full-scale figure. b) Zoomed region of samples with small mass change.

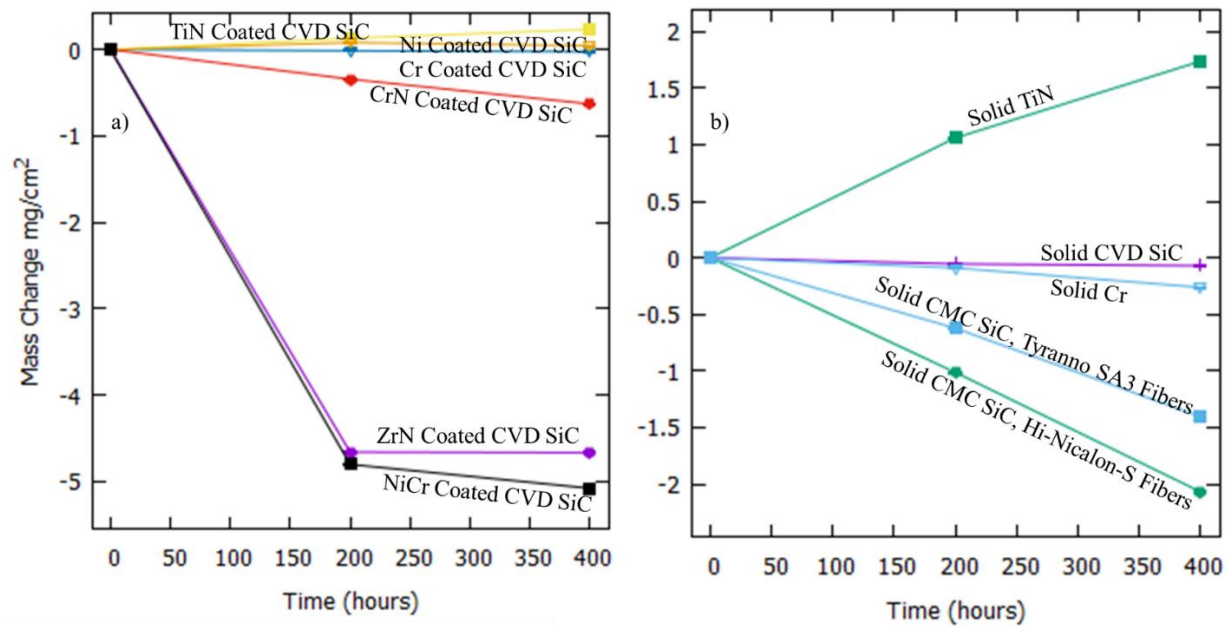


Figure 4.13: Mass change of specimens exposed to BWR-NWC conditions for 400h. a) Coated CVD SiC specimens. b) Uncoated SiC and monolithic coating materials.

larger mass changes in both directions. In both conditions TiN coatings behaved similarly to the pure TiN samples, except that the high porosity of the solid TiN led to enhanced mass loss. The ZrN and NiCr samples immediately spalled from the surface, as in HWC. Following the initial spallation, mass loss proceeds slowly, as expected for CVD SiC. For reasons discussed in section 6.2.3, the ZrN, Ni, and NiCr coatings were not considered further in this work. Additionally, CMC SiC was not further exposed to autoclave conditions, but was included in the exposures at the MITR, as discussed in chapter 3. Images of all these samples are reported in Appendix A.

4.2 Exposures of Uncoated SiC in the Absence of Irradiation at ORNL

4.2.1 As-prepared Specimens

As-prepared surfaces of both polished and as-cut samples were examined by SEM and AFM to obtain a benchmark against exposed specimens. Representative AFM and SEM-BSE images are given in Figure 4.14 and Figure 4.15, respectively. Both figures show a smooth surface for the polished SiC. In Figure 4.15, it is observed that many large grains are grown with small grains interspersed between them. Individual grains cannot be observed in the as-cut samples due to their roughness. Surface maps were used to evaluate true roughness as compared to projected (geometrically calculated) area. This revealed a 2% correction for polished samples and a maximum of a 35% correction for as-cut (unpolished) samples.

True surface area was determined using a series of AFM scans with differing x-y resolutions. Due to the limited size of AFM scans 2-4 sites were examined for statistical analysis. The maximum surface area was then estimated by using the evaluations at 2.5 nm x-y resolution, where the surface area was observed to peak in the unpolished samples (Figure 4.16).

4.2.2 Mass Change and Electron Microscopy

Mass change data from deoxygenated tests is presented in Figure 4.17 for both polished and as-cut sample types. Comparing the data in each of the three conditions, there was not a statistically significant difference between the points either with time, or across the studies. A positive correlation of mass loss rate with temperature is inferable within the relatively large signal error. This error is due to the low magnitude of the mass change, the error bars and corresponding signal-to-noise ratios are quite large. Unpolished sample data are given in two lines, dashed and solid. The difference between these represents a correction to the maximum expected true surface area compared to the geometric approximation (projected area). Per the AFM data from section Figure 4.16, a 35% increase in the surface area for the unpolished specimen was applied when calculating the mass change. In each condition, the polished and unpolished samples lost a nearly equivalent amount of material, within the error. Moreover, within the error, the mass change can be presumed linear, for purposes of kinetics analysis.

Scanning electron microscopy (SEM) using backscatter electrons (BSE) and energy dispersive spectroscopy (EDS) was conducted and is shown for the surfaces of a sample from each exposure condition in Figure 4.18. These figures are quite similar to the reference specimens, (c.f. Figure 4.15), with no clearly observable grain boundary attack and no grain fallout. Some increased brightness is observed in Figure 4.18d, this is not grain boundary attack, as examined

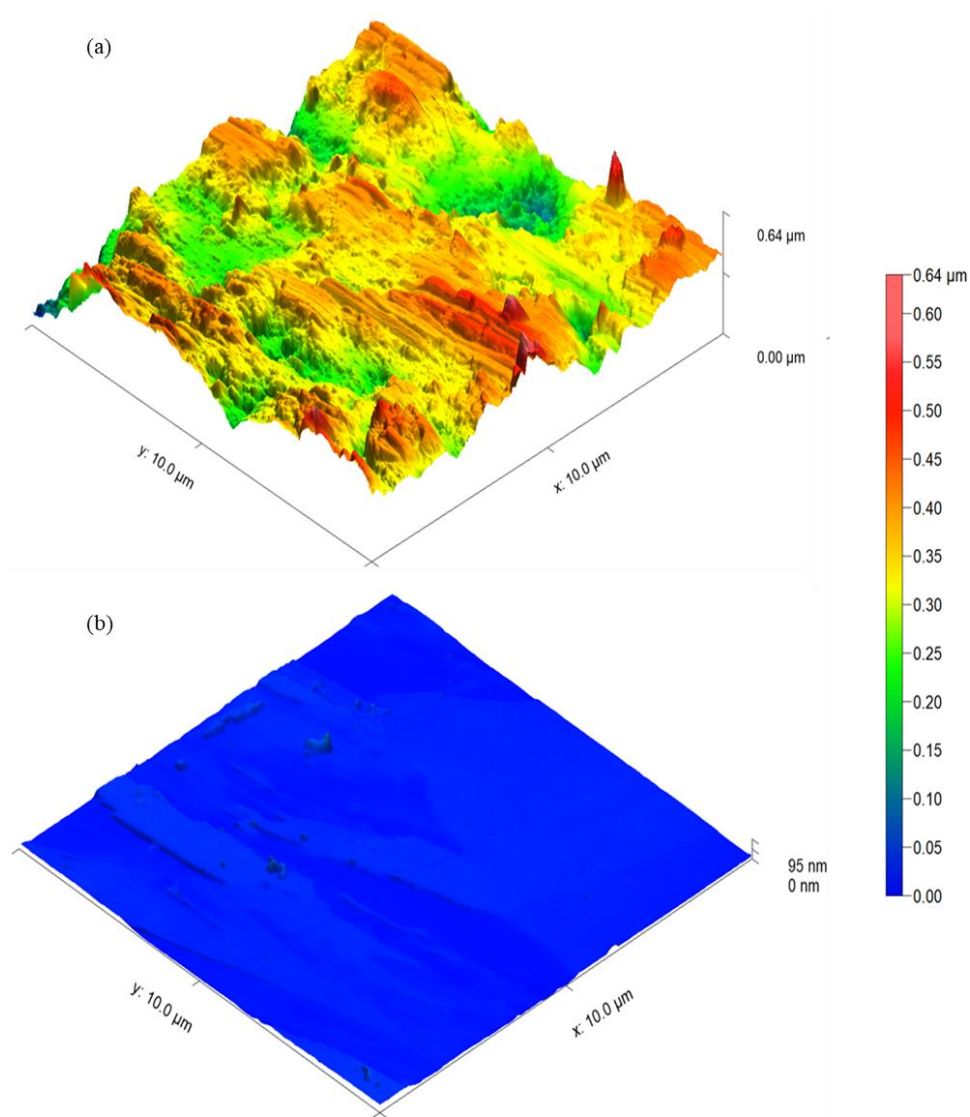


Figure 4.14: Representative atomic force microscopy (AFM) topographical maps of (a) as-received (unpolished), and (b) polished SiC prior to examination. Both images use the same scaling. Reproduced from [136].

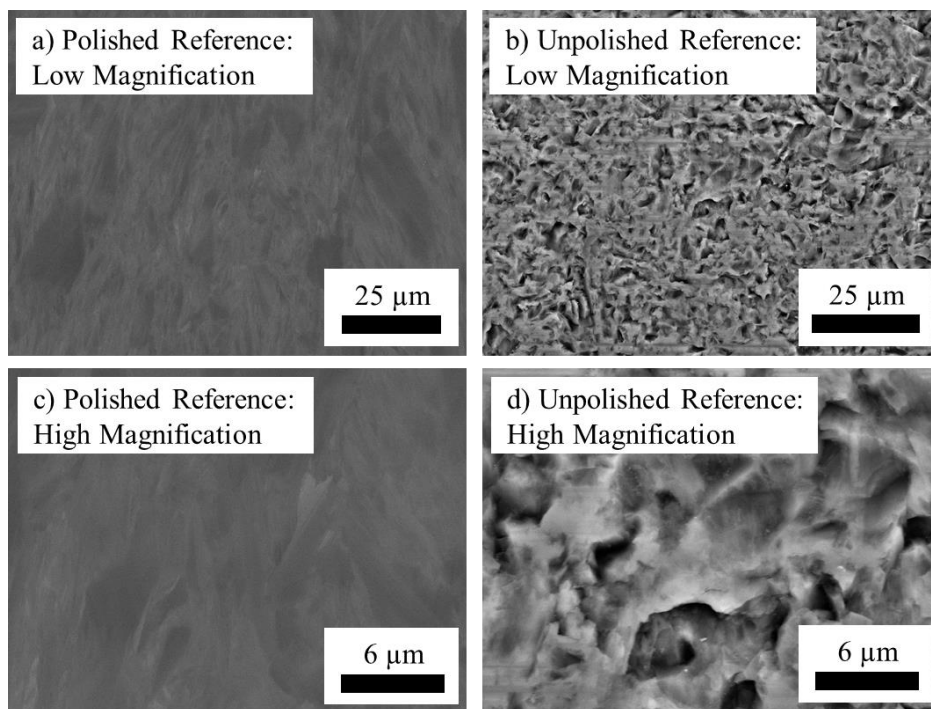


Figure 4.15: Representative SEM-BSE images of the surfaces of polished (a and c) and as-cut (unpolished, b and d) SiC samples without any exposure at low (a and b) and high (c and d) magnification.

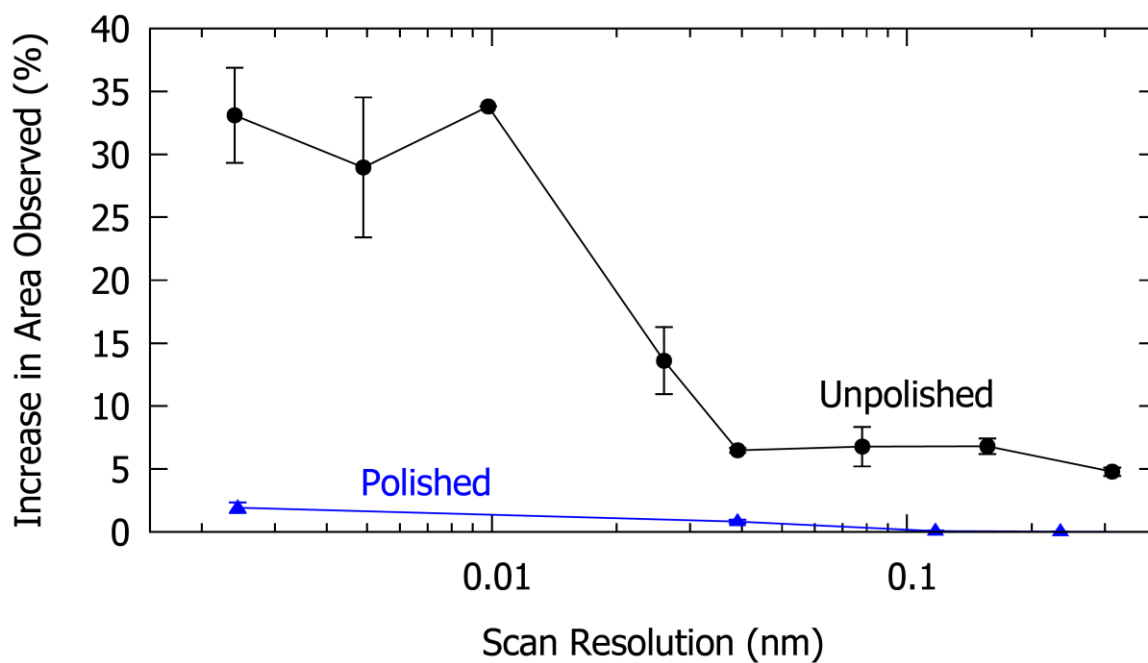


Figure 4.16: Increase in observed surface area of both the as-cut (unpolished) and polished SiC samples beyond geometric surface area, expressed as a percent. The x-axis represents the distance between sampling locations (i.e, 1 nm resolution corresponds to 10^6 points in a $1\mu\text{m} \times 1\mu\text{m}$ scan). Lines are labeled appropriately.

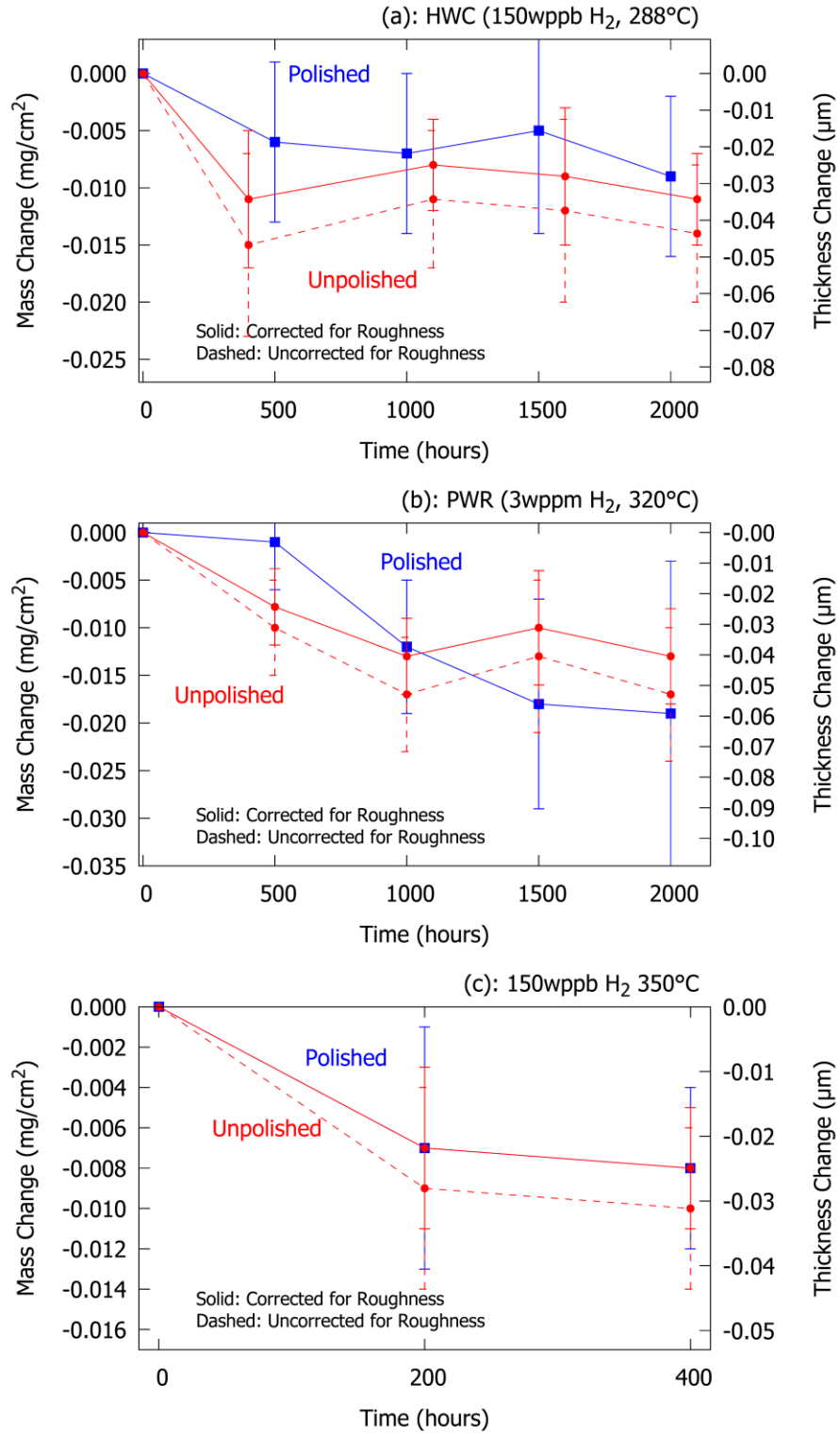


Figure 4.17: Average mass change per area of samples exposed in a) BWR-HWC conditions (288°C, 150 ppb H₂), b) PWR (320°C, 3ppm H₂), and c) 350°C, 150 ppb H₂. Data corresponding to polished samples in shown in solid blue and labeled. Unpolished samples are labeled and shown in red using both geometric area determinations (dashed lines), and geometric area corrected for surface roughness (solid lines).

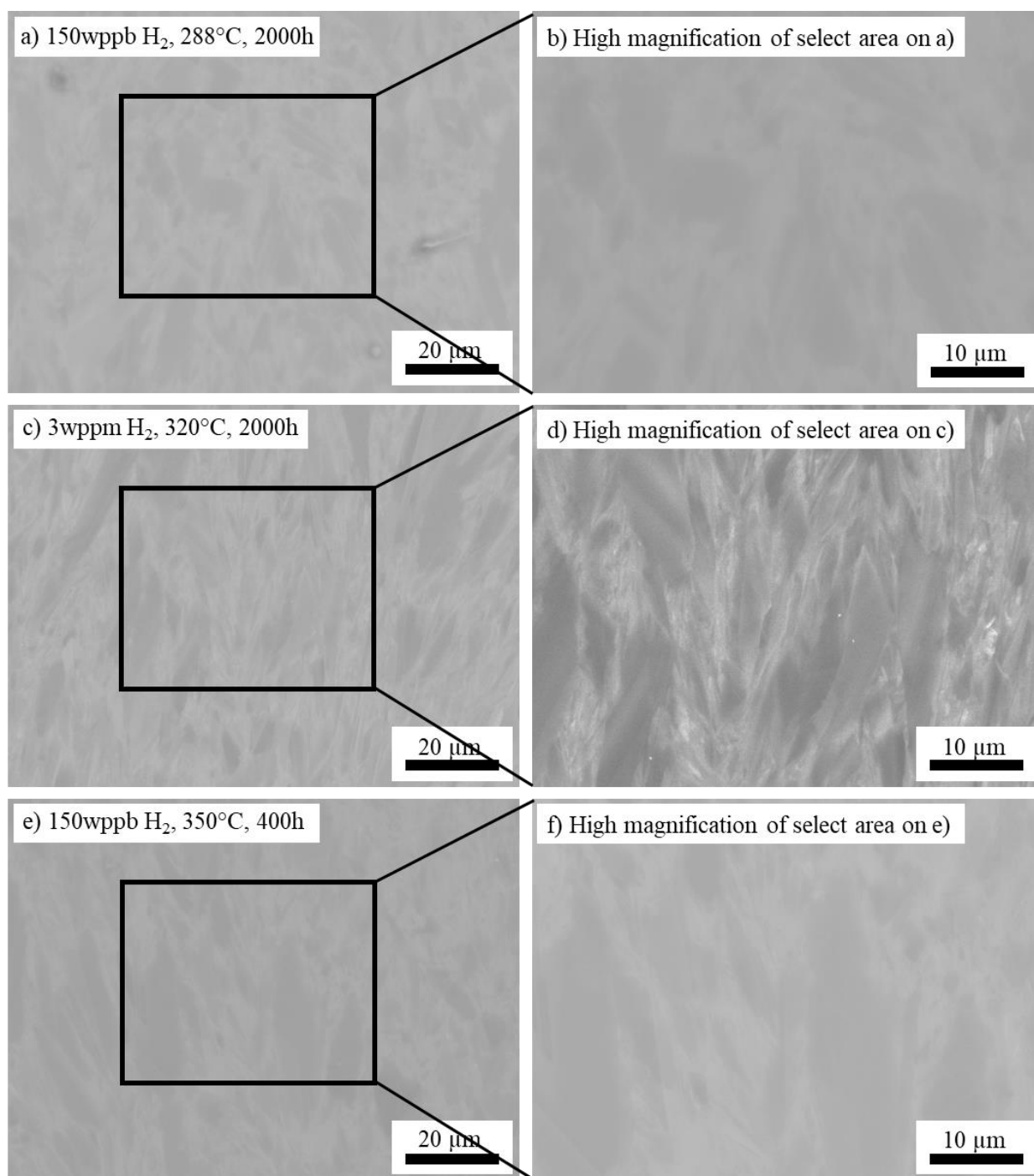


Figure 4.18: SEM-BSE of samples exposed in all three deoxygenated tests. a), c), and e) represent the HWC, PWR, and 350°C at 150wppb H_2 samples, respectively. b), d), and f) represent a zoomed area of the center of a), c), and e), respectively.

by AFM, but may correspond to small-crystallite deposition from the autoclave solution (c.f. deposits in Figure 4.20).

The mass change of samples in select oxygenated conditions is presented in Figure 4.19, with polished and unpolished data sets presented as in the deoxygenated case. Unlike the deoxygenated conditions, the polished samples corroded substantially more slowly than the unpolished samples, regardless of condition (although in Figure 4.19c, the last data points are statistically overlapped). This effect remains even after accounting for the additional area. Generally, the lowest temperature tests corroded the SiC the slowest, with the largest degradation at higher temperatures, including more rapid onset of nonlinearities. Additionally, increasing oxygen concentration in the water increased the corrosion rate as well.

In a), the NWC condition, both types corrode linearly within the error, with the unpolished samples exhibiting roughly a factor of two higher mass loss rate. Nonlinearity begins between 400 and 600 hours in the polished specimens at 350°C with 1wppm O₂, b). Nonlinearity is also present in the unpolished samples, but is less well pronounced. In c) the increase of oxygen content to 4wppm significantly increases these nonlinearities. Following 200h, the polished samples trend becomes clearly nonlinear (linearity prior to this point was confirmed with a second follow-up test for 50h, as shown in the figure). This also occurs for the unpolished samples and is particularly clear following 400h. As with Figure 4.19a) and b), in the first 200h the polished and unpolished samples corroded at different rates (higher corrosion for the unpolished sample). However, in the final 2 exposures, both types lost mass at approximately at the same rate, within the sample area, when the initial surface area is corrected.

These observations were also reflected in the sample microscopy. SEM-BSE images of the polished sample surfaces following exposure are presented in Figure 4.20. Following 2000h in the NWC condition (a and b), significant grain boundary attack is evident along with fallout of small grains. Similarly, grain boundary attack is observed at 350°C at 1wppm O₂ following 600h of exposure (Figure 4.20c) and at 2wppm O₂ following 100h of exposure (Figure 4.20d). In comparison, following 600h in 4wppm O₂ at 350°C (Figure 4.20d and e), more fallout is visibly observed. In each of the micrographs in Figure 4.20c-e, many bright white particles are observed on the surface. These were confirmed by EDS to be oxides containing Ni and Fe, implying deposition of metallic oxides from the solution. Each protruded off the surface of the samples exposed to 350°C oxygenated conditions and were only observed to be substantial for the long exposures under these conditions (600h). In this case, using the cross-sectioned samples, these particles were estimated to account for a mass addition of ~0.03 mg/cm² on these samples, on the order of the experimental error in these tests.

Cross sections of relevant samples are shown in Figure 4.21 for oxygenated tests. In each of the observed micrographs, grain boundary attack penetrates up to 4 microns into the sample, with the degree of attack being substantially greater at longer exposure times (compare Figure 4.21b and c). A micrograph of the polished reference is also provided, showing a smooth surface. EBSD was attempted on the cross-sectioned samples, but suitable patterns on the edge of the sample were not obtainable. This is due to the fact that SiC and epoxy polish at different rates, leading to a slight gradient at the epoxy/SiC interface, which is enough to make analysis of grains not

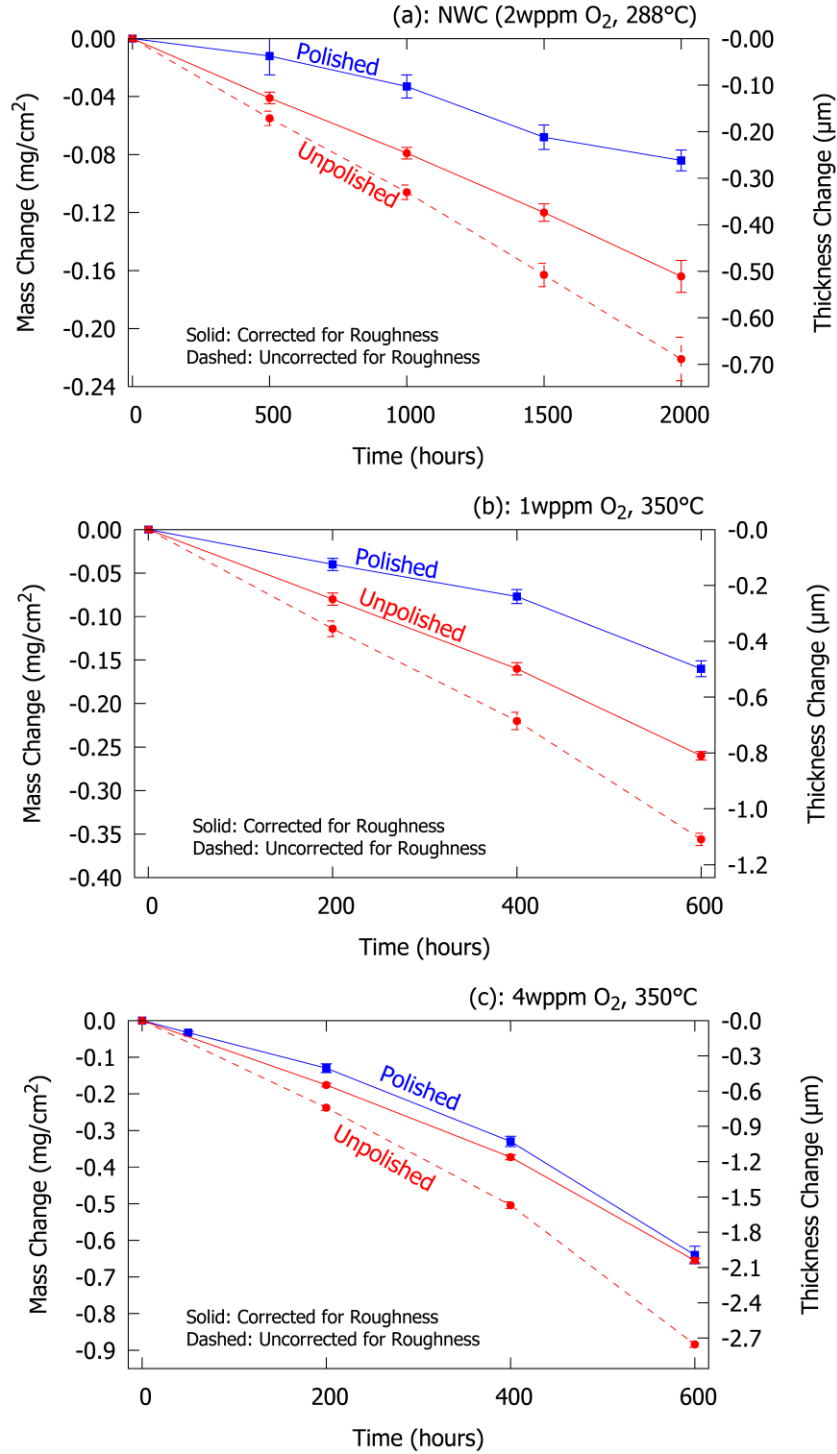


Figure 4.19: Average mass change per area of samples exposed in a) NWC conditions (288°C, 2ppm O₂), b) 1ppm O₂, 350°C, and c) 4ppm O₂, 350°C. Data corresponding to polished samples is shown in solid blue and labeled. Unpolished samples are labeled and shown in red using both geometric area determinations (dashed lines), and geometric area corrected for surface roughness (solid lines).

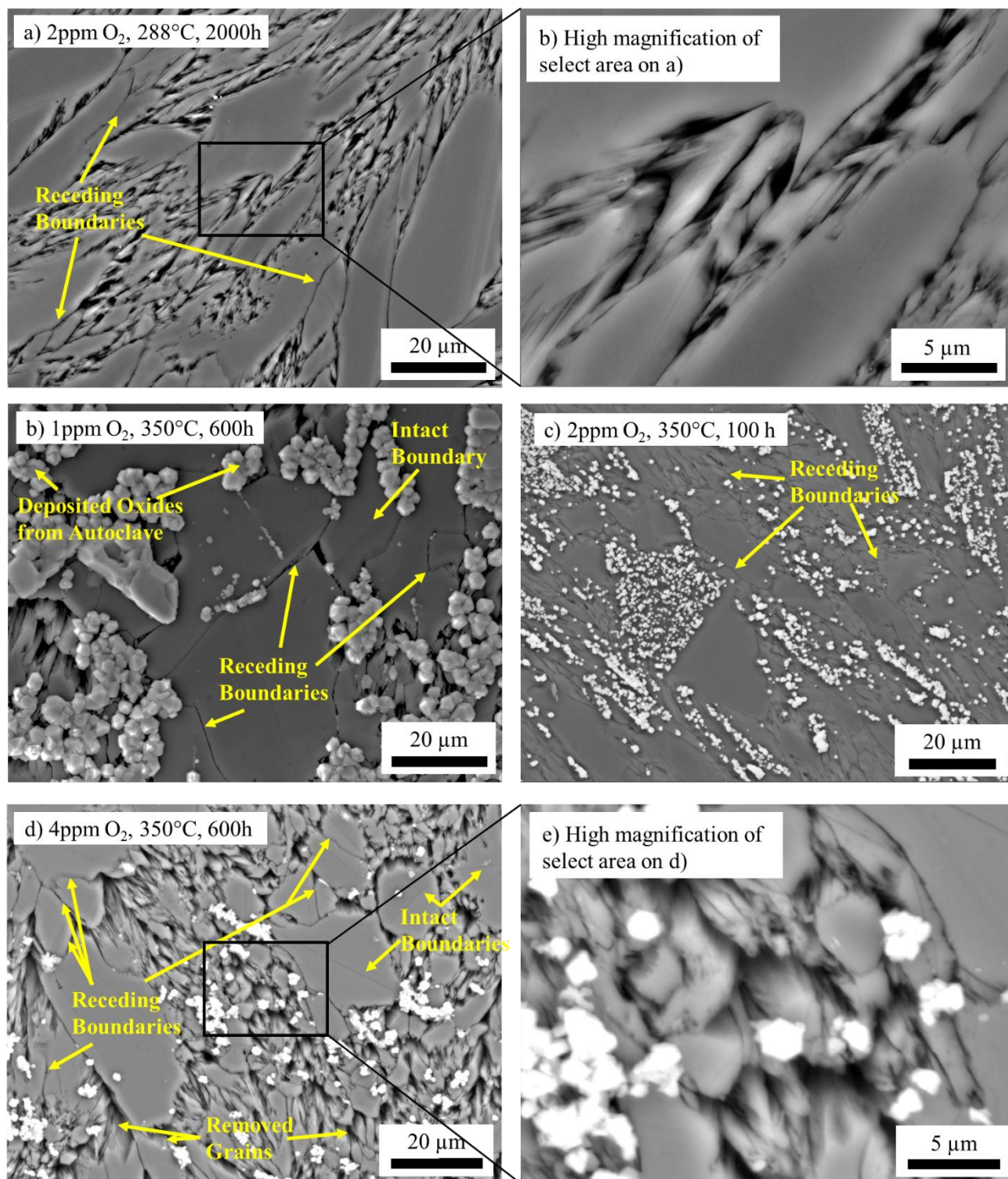


Figure 4.20: SEM-BSE images of the surface of samples exposed in oxygenated tests. a) and b) represent low and higher magnification images of samples exposed to 2000h of NWC (2ppm O₂, 350°C). c) shows the surface of a sample exposed to 600h of 1ppm O₂, 350°C

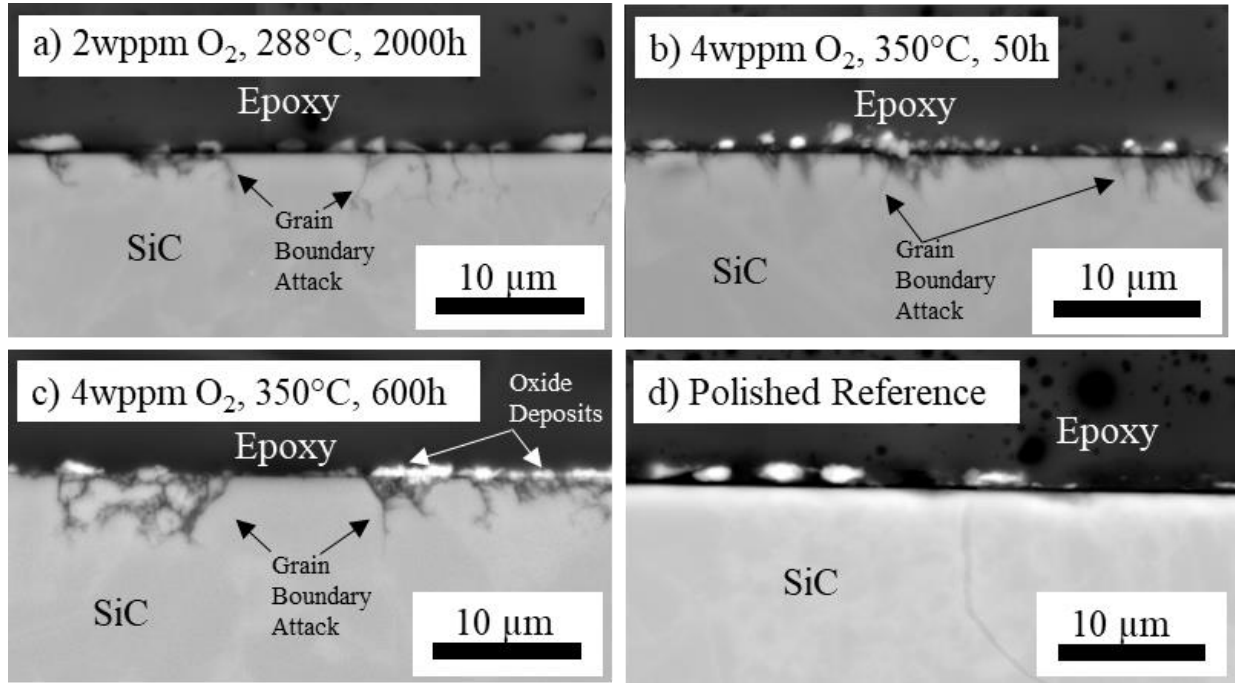


Figure 4.21: SEM-BSE micrographs of cross-sectioned CVD SiC samples a) exposed to NWC conditions (2ppm O₂, 288°C) for 2000h, b) 4ppm O₂, 350°C for 50h, c) 4ppm O₂, 350°C for 600h, and d) an unexposed polished reference.

feasible from this work. As such, no quantification of grain boundary attack relative to misorientation angle and grain boundary character is possible in this work. Because of the extent of the attack observed in cross-section, which clearly is not short or straight and perpendicular to the surface, AFM was not used to quantify grain boundary recession in oxygenated samples. Grain boundary attack was not observed in deoxygenated conditions by AFM and selective recession of particular grain orientations was not observed.

4.3 MITR Exposures of Uncoated SiC

4.3.1 Mass Change

Pre-test and post-test mass measurements from ORNL and MIT were averaged to determine an estimate of mass error. A summary of the mass change data for the various test conditions is reported in Figure 4.22 and Figure 4.23. Figure 4.22 compares individual sample mass changes for all three polycrystalline CVD SiC sample types in each exposure condition. In Figure 4.23, the R&H CVD variant is compared to the single crystal and CMC variants. In each, thickness change was calculated from the mass loss data by assuming uniform mass loss across the surface. The previous results (as well as literature observations) show that any localized attack should take the form of grain boundary attack (possibly some pitting) and is typically associated with low resistivity samples and/or oxygenated conditions. Therefore, unless such attack is observed, uniform mass loss may be assumed for CVD SiC. As shown below, in this study localized attack of sufficient magnitude to affect this assumption was not observed. With CMC SiC, this assumption will not likely be valid, as will be discussed later. For purposes of comparison, however, it is included in the figures.

These figures show an increase in the mass loss of all samples with the addition of radiolysis, and a further increase when adding neutron radiation damage. The tested CMC samples lost significantly more mass than the CVD or single crystal samples in all conditions and the water-only CMC sample was the only one to gain mass over the course of the exposure. Excepting the CMC sample, error in all the samples is close to the value of mass loss for water-only exposures. A higher signal-to-noise ratio is observed in the radiolysis-exposed CVD samples due to the additional mass loss for those samples. The samples in the radiolysis-only condition were statistically equivalent. Statistically significant differences are apparent between the HR2 and HR sample types exposed in the core. The data from the present 127 day exposure (linearly extrapolated) implies a maximum thickness recession in CVD SiC of about 5 μm over the course of 5 years under the present conditions. The measured corrosion for the CMC sample was higher than the other samples for both the radiolysis and neutron damage conditions, with a maximum recession estimate of 120 μm obtained by linear extrapolation to 5 years of the measured mass loss.

4.3.1 Microscopy

The samples were characterized with SEM. Examination of the surfaces of samples in the core, above the core, and out of the core is presented in Figure 4.24. Out-of-core and above-core samples were free of any features associated with localized attack, even at higher magnification. In contrast, extensive and uniformly distributed localized attack was observed on all in-core samples, regardless of manufacturer or batch. However, there was some difference in the

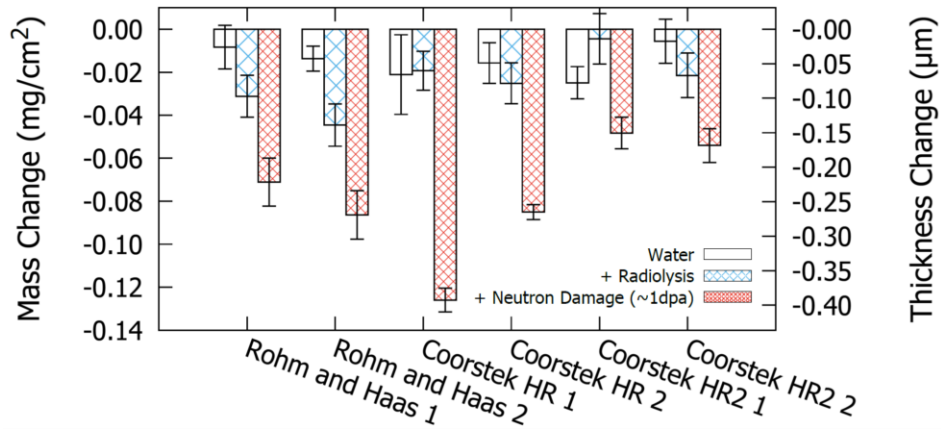


Figure 4.22: Individual sample mass change for high resistivity polycrystalline CVD SiC from the MITR loop experiments. All six samples of each type are included. The 1 and 2 after each sample designation distinguished between the two samples of each type included in the test.

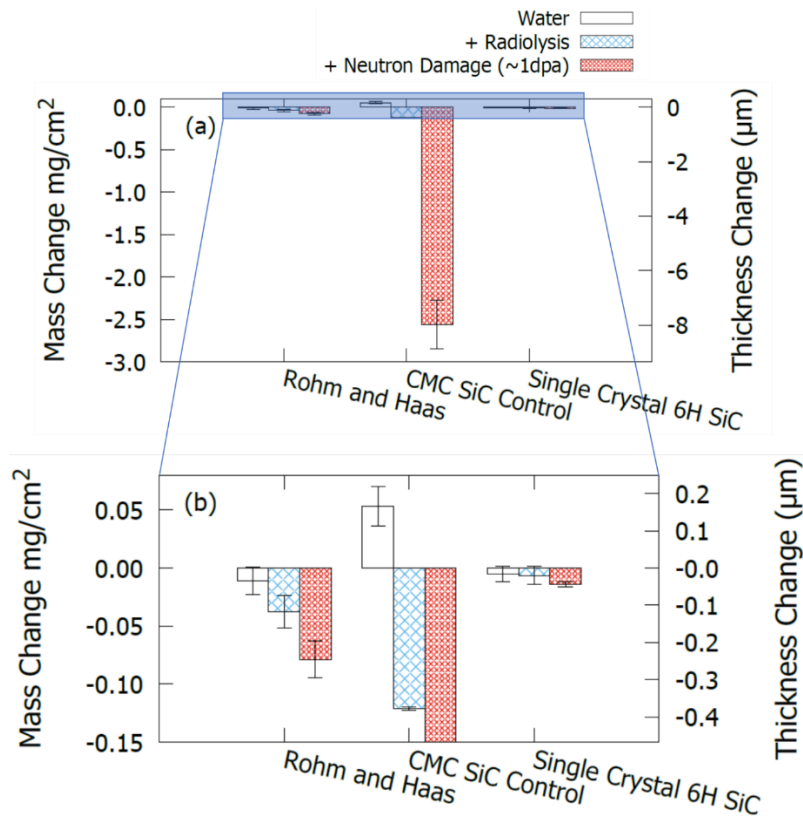


Figure 4.23: Average sample mass change of both R&H CVD SiC samples in each condition., 6H SiC, and CMC SiC. The full range plot is given in (a) with the boxed area expanded in (b) for clarity. Thickness change is estimated by assumption of uniform corrosion change.

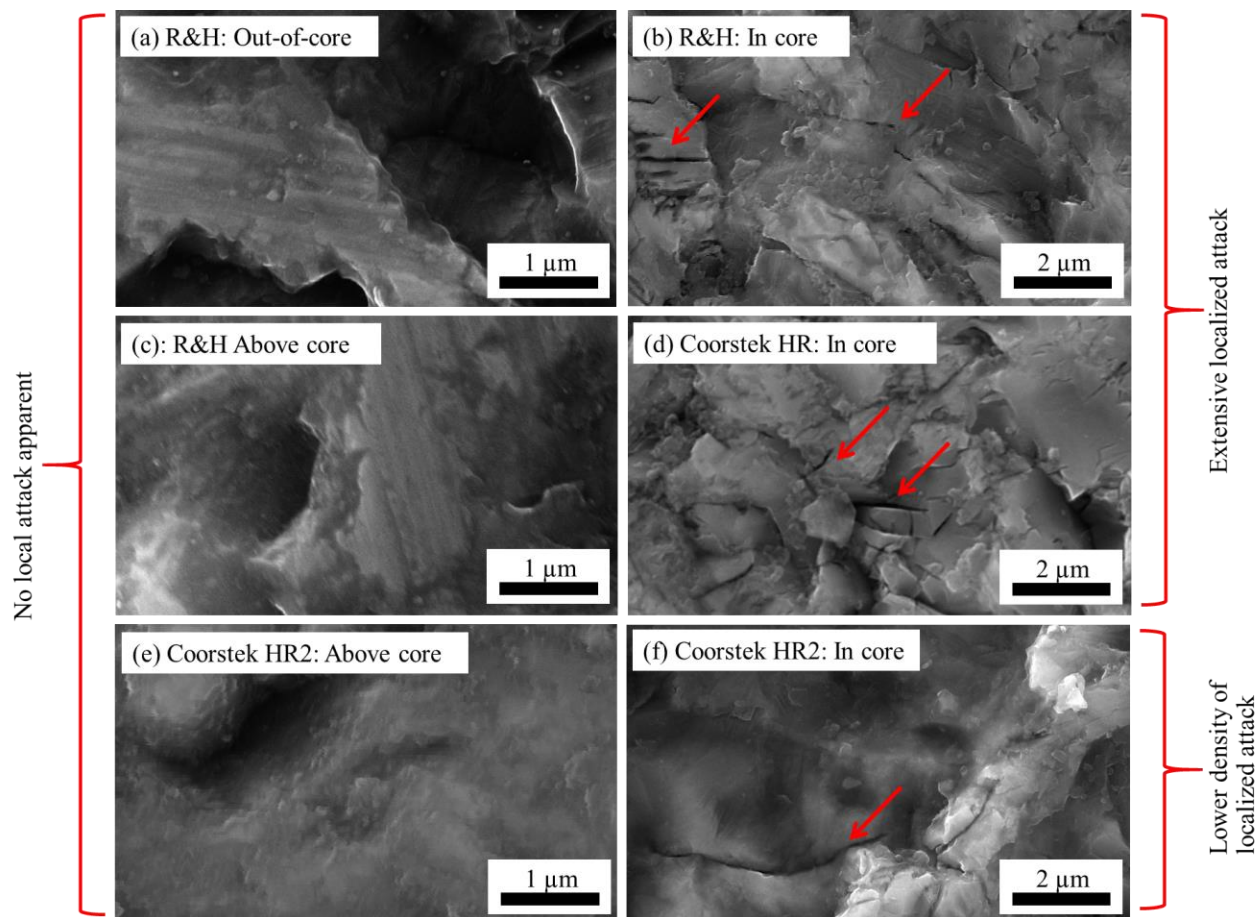


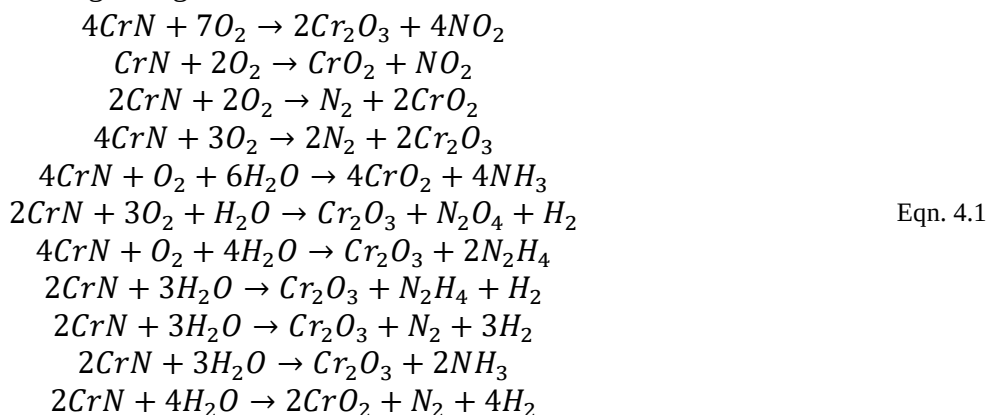
Figure 4.24: SEM images of CVD R&H SiC (a) out of the core. (b) in the core, and (c) above the core. (d) Coorstek CVD HR SiC in the core. Coorstek CVD HR2 SiC (e) above core and (f) in the core.

apparent density of attack sites dependent on sample batch. The R&H and Coorstek HR sample visually had similar groove densities which were about 2-3 times that of the Coorstek HR2 sample in core. This is consistent with the smaller mass loss of the Coorstek HR2 SiC as opposed to the other samples in the core. To determine whether the attack was correlated to grain boundaries, EBSD was conducted on cross-sectioned samples; the inherent roughness of the samples was too great to perform EBSD on as-exposed samples. However, while EBSD could be conducted in cross-section, the samples were not smooth enough to observe surface attack in cross-section (and thus no correlations to underlying microstructure were possible).

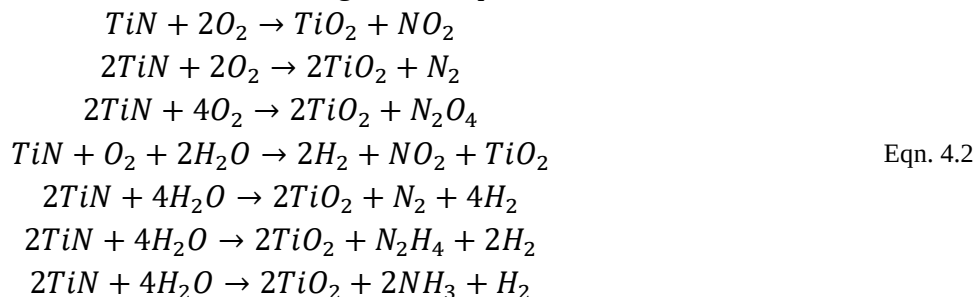
4.4 Exposure of Coatings in the Absence of Irradiation at ORNL

4.4.1 Pourbaix Diagrams of Coating Materials

Pourbaix diagrams were constructed for Cr, CrN and TiN materials using FactSage 7.2TM. In the case of Cr, this is straightforward using the standard conditions of defining all metallic species as having a concentration of 10^{-6} M. For the ceramic species, an additional constraint is required, coming from the nitrogen in the ceramic, which will naturally enter into the solution as well. This is non trivial, since it also involves choosing a primary reaction product as a result of the CrN and TiN reaction. To illustrate this, Eqn. 4.1 shows a variety of thermodynamically viable reactions of CrN with oxygen and/or water. An examination of these possibilities reveals 5 reaction products including nitrogen: N_2 , NO_2 , NH_3 , N_2O_4 , N_2H_4 .



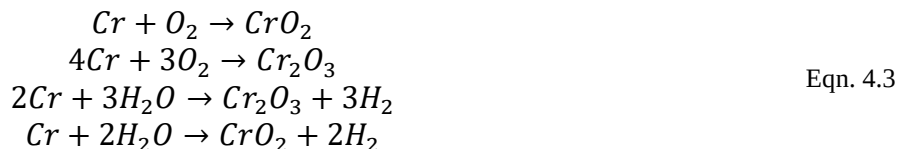
The same list results from reactions with TiN, given in Eqn. 4.2.



In construction of the diagram, any of the nitrogen-containing products could be chosen to determine the equilibrium line locations. However, the most reasonable of these is N_2 given its

preponderance in air and lack of reactivity. Thus, the Pourbaix diagrams of TiN and CrN are given in Figure 4.25 and Figure 4.26 using $[N_2]=1 \times 10^{-6}$ M. As noted, the N-containing products

are not relevant for the reactions of Cr, the most likely of which is given below. Figure 4.27 gives the Pourbaix diagram of Cr, similar to diagrams found in [137].



The diagrams of Cr and CrN are quite similar, showing identical reaction products, as expected and only differing in an additional 300-400mV range of protection for the CrN. In all oxygenated cases, indicated by red triangles, the potential is high enough that no thermodynamic protection is offered. Critically, this implies nothing about the possibility of kinetic protection (where the reaction rates are low enough that the thermodynamic instability does not matter).

Thermodynamic protection is offered, however, in the deoxygenated cases (represented by the circles, green for ORNL autoclave, black for MITR) and Cr_2O_3 is eventually expected to form. However, Cr_2O_3 is not the only stable corrosion product near the deoxygenated conditions. By ignoring Cr_2O_3 in the calculation, and then also ignoring Cr_3O_4 (another stable oxide), it is shown that another oxide, CrO_2 is a thermodynamically stable product, at least under high temperatures. The usefulness of this observation is shown in section 4.4.3 and discussed in 6.5.2. TiN is far less interesting. Under all conditions of relevance it is expected to react to TiO_2 , which is stable. Thus, passivation is expected absent spallation.

4.4.2 Mass Change

The calculated mass change per area of all coating types is given in Figure 4.28-Figure 4.30. In each figure, an approximate uniform thickness change is estimated using the density of the coating material. The multilayer Cr/CrN coating is shown Figure 4.28. As shown there, in both reaction conditions the coating lost mass equivalent to 12-15 μm , which is the entire coating thickness. As a consequence, the multilayer Cr/CrN was not included for additional testing here. However, these tests were performed in parallel to the MITR exposures, the results of which are given in section 4.5.

The mass change of the remaining coating types, Cr, monolithic CrN, and TiN is given in Figure 4.29 for oxygen exposures. Under both NWC (288°C and 2wppm O_2) and under 350°C and 1wppm O_2 each coating lost significant mass without any evidence of passivation. Exposed to NWC the Cr coating (a) did not initially loss much mass, but between 600 and 1600h the entire coating spalled (and was thus not included for the final 1000h of exposure). In the 350°C, 1wppm O_2 exposure full spallation was not observed, but the sample did lose significant mass with an increasing rate with time. The CrN samples (b) reacted much more slowly than the Cr, and even gained mass initially at the higher temperature. However, by the end of the 2400h exposure, the sample had a net mass equivalent to 1.6 μm of uniform thickness recession. In contrast, the TiN samples (c) initially oxidized at similar rates in both oxygenated conditions. However, following 400h at 350°C, 1ppm oxygen and 600h in NWC conditions, the TiN began to spall, removing the entire coating. As such, the TiN samples were also not included in the final 1000h of testing. Images of these coatings is provided in Appendix A. Mass change in the absence of oxygen is shown for each coating in Figure 4.30. Unlike the

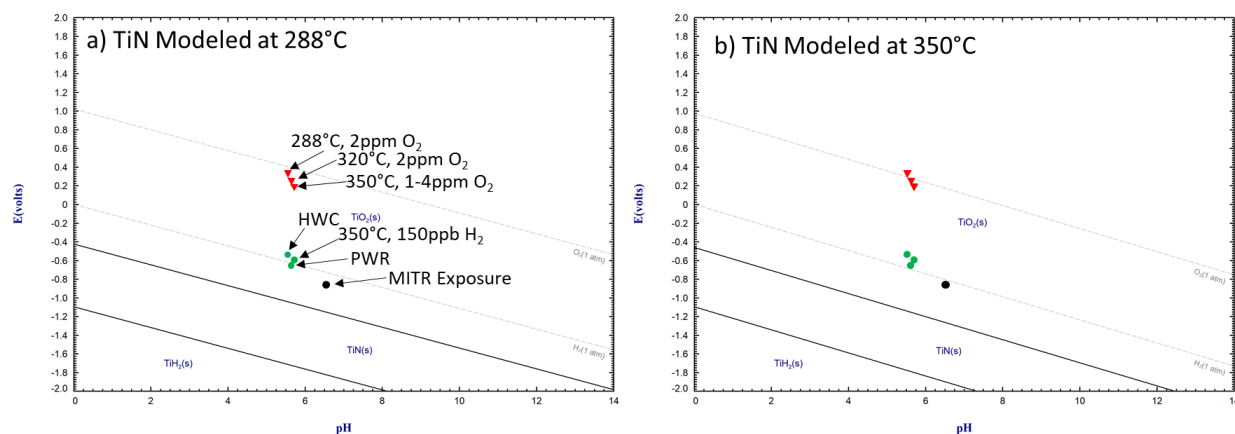


Figure 4.25: Pourbaix diagram of TiN in water as calculated by FactSage 7.2. The LWR-simulating conditions are given by points on the diagram, per Table 3.2 and Table 3.3. a) and b) represent the diagram at 288 and 350°C, respectively.

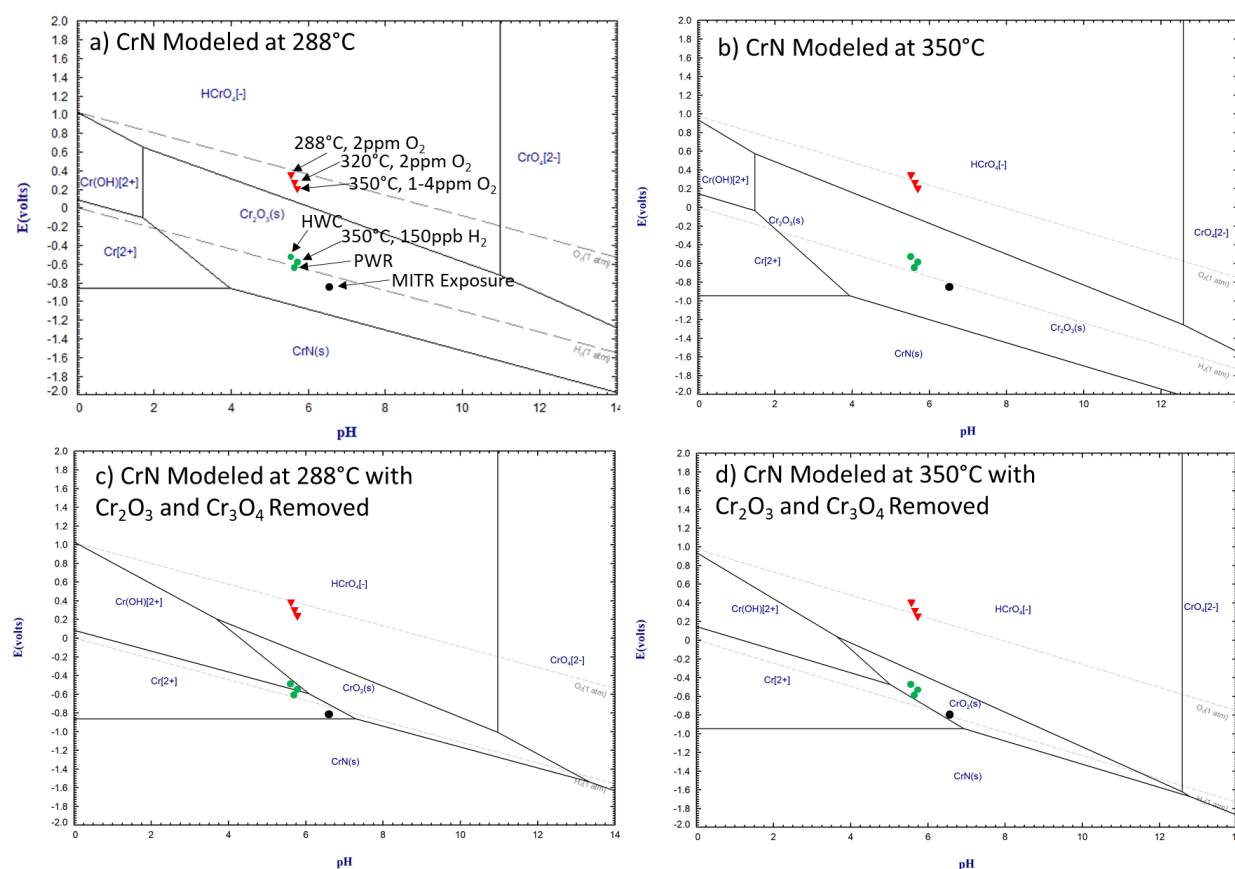


Figure 4.26: Pourbaix diagram of CrN in water as calculated by FactSage 7.2. The LWR-simulating conditions are given by points on the diagram, per Table 3.2 and Table 3.3. a) and b) represent the diagram at 288 and 350°C, respectively. c) and d) are the same systems with Cr_2O_3 and Cr_3O_4 removed from the calculation.

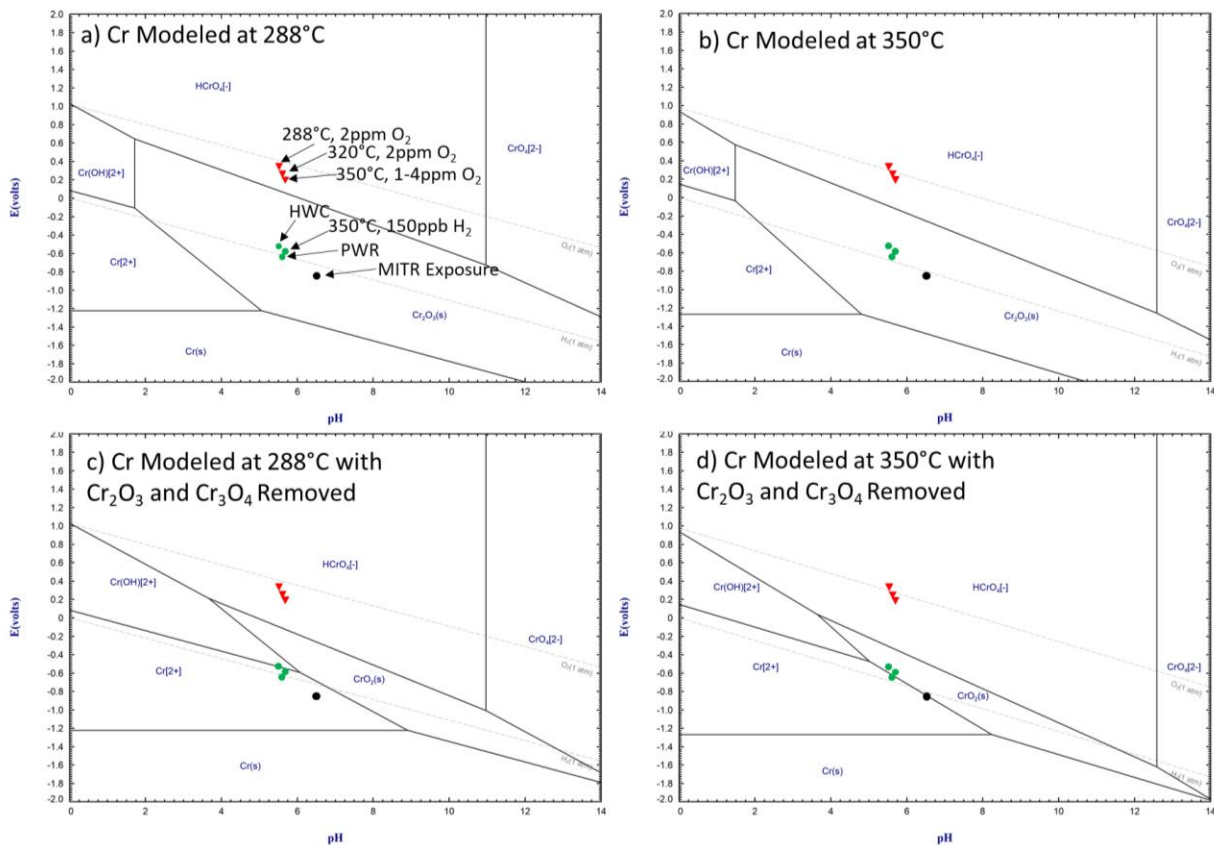


Figure 4.27: Pourbaix diagram of Cr in water as calculated by FactSage 7.2. The LWR-simulating conditions are given by points on the diagram, per Table 3.2 and Table 3.3. a) and b) represent the diagram at 288 and 350°C, respectively. c) and d) are the same systems with Cr_2O_3 and Cr_3O_4 removed from the calculation.

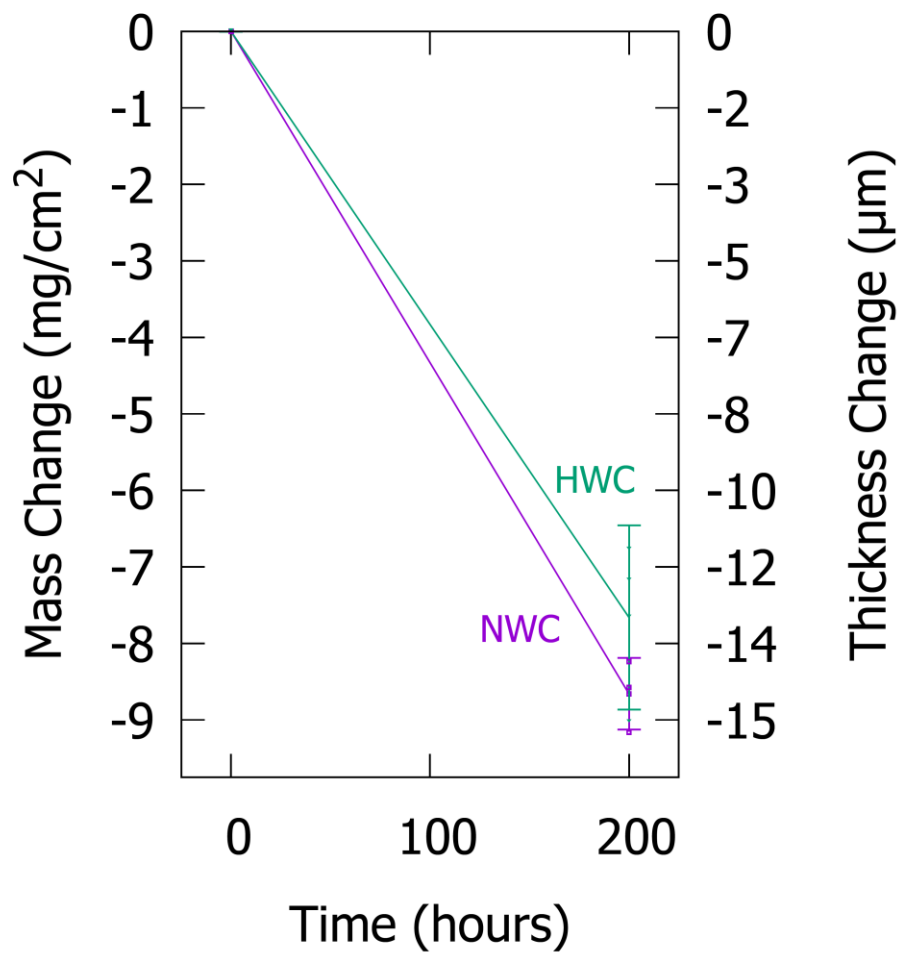


Figure 4.28: Mass change of multilayer Cr/CrN coatings exposed to BWR-HWC and BWR-NWC conditions. Labels and colors on the graph indicate which data belongs to which condition.

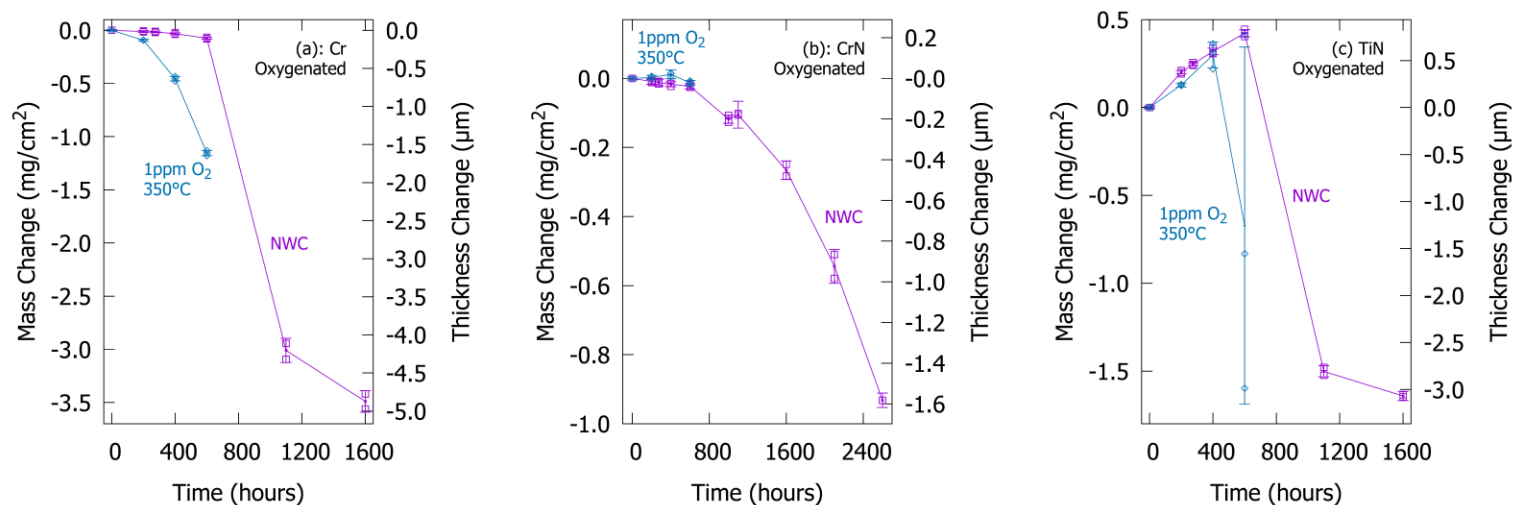


Figure 4.29: Mass change plots of Cr (a), monolithic CrN (b), and TiN (c) in oxygenated environments. Labels on the plot show indicate which lines belong to which condition.

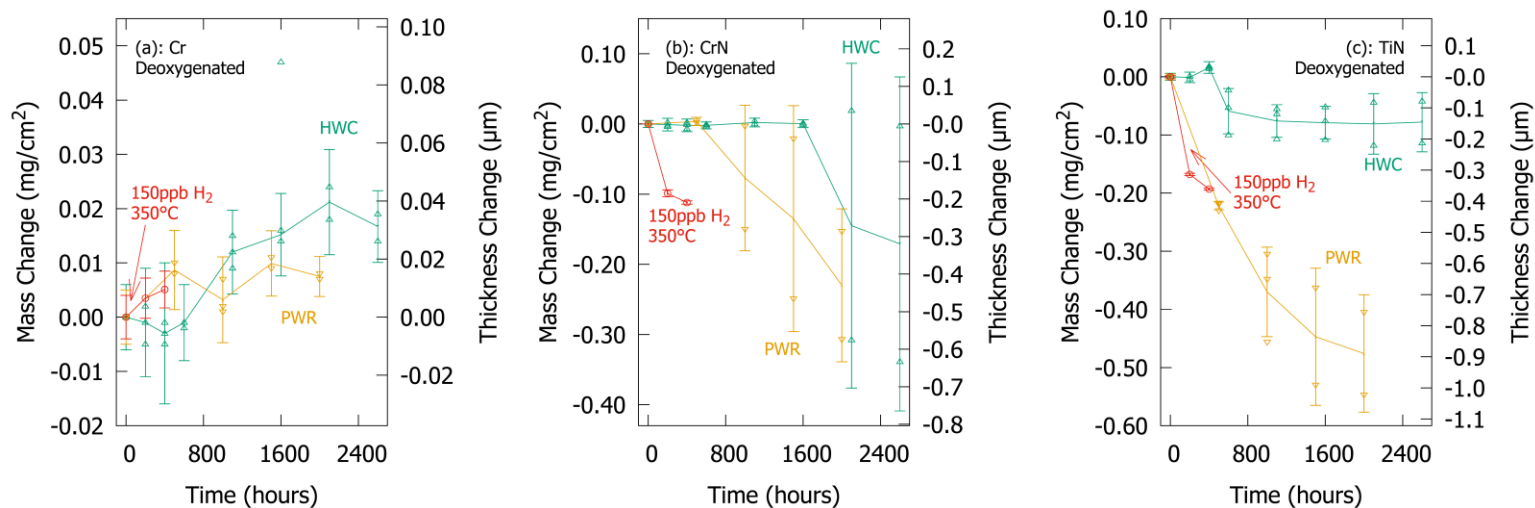


Figure 4.30: Mass change plots of Cr (a), monolithic CrN (b), and TiN (c) in deoxygenated environments. Labels on the plot show indicate which lines belong to which condition.

oxygenated conditions, Cr (a) gains a small amount of mass in each of the three conditions. Mass changes are statistically equivalent across the ranges of exposure and amounted to up to 40 nm of oxide gain, uniformly across the surface. Initially, the HWC-exposed CrN samples also were protective and did not lose any mass (Figure 4.30d). However, after 1600h, some localized spallation was observed on one sample, leading to loss of material. The onset of spallation was decreased with increasing temperature and began after 600h and 200h in PWR and 350°C with 150ppb H₂, respectively. The TiN samples behaved similarly (Figure 4.30c). Up to 600h in HWC, TiN gained some mass. Between 400h and 600h, all samples lost some mass, and one of the remaining samples continued to lose mass, while the other slightly gained mass. In the higher temperature conditions mass loss onset in the first exposure period and continued through the duration of the exposure. In PWR, by 2000h, about 30% of the coating was removed.

4.4.3 Raman Spectroscopy of the Surfaces

Raman spectra of the as-exposed surfaces are presented for TiN, CrN, and Cr, in Figure 4.31-Figure 4.33, respectively. Exposure conditions and length, along with sampling locations (as relevant) are given on the figure. A reference spectrum is included in each graph as well. Non-reference peaks are identified as TiO₂ (anatase or rutile), or (Ni,Fe)TiO₃ for the TiN-coated samples and Cr₂O₃, CrO₂, or general spinel for Cr and CrN-coated samples. These peaks were identified using [134, 138-150]. SiC peaks were identified using the peaks for the reference SiC, given in section 4.1.3. A specific spinel is not identified in the figures because there is not sufficient evidence to discriminate between different possible spinels as a result in similarity of candidate structures and the inherent noise in the data. As shown in the next section, both Fe and Ni-rich oxides were found precipitated on the surface, suggesting spinels specifically of the form (Fe,Ni)Cr₂O₄. This is discussed further in section 6.5.

From Figure 4.31, TiN forms the anatase phase of TiO₂ in deoxygenated conditions and no TiN peaks are observed. Oxygenated water removes much of the coating, leading to observation of only SiC peaks on the surface. However, near the edge of the sample exposed to 350°C and 1ppm O₂ for 600h, where some of the coating was still adherent, both rutile and anatase phases of TiO₂ were observed with the bulk of the peak intensity coming from rutile. Additionally, in the HWC sample alone, several non-TiO₂ peaks were observed, consistent with an (Fe, Ni)Ti₂O₃ structure.

Raman of CrN, shown in Figure 4.32, shows rather low signals of non-spinel oxides in all conditions and locations. At 2000h and 2600h in PWR and HWC, respectively, peaks of CrO₂ and Cr₂O₃ are observable and CrO₂ may be convolved with the left tail of the ~700cm⁻¹ spinel peak. Localized spallation within the sample led to one observation of SiC substrate on the sample exposed to PWR conditions for 1000h. On the coating edge of the sample exposed to 1ppmO₂, 350°C for 600h the spinel peaks were not discernable and were replaced with the peaks of CrO₂ and Cr₂O₃. Further, the CrO₂ peaks are the most intense. However, the number of peaks combined with their apparent broadness makes a baseline difficult to discern, particularly in the 400-700 cm⁻¹ range. These observations are quite similar to those on the Cr samples. However, a few points are different. First, more spallation led to additional regions where the SiC substrate is

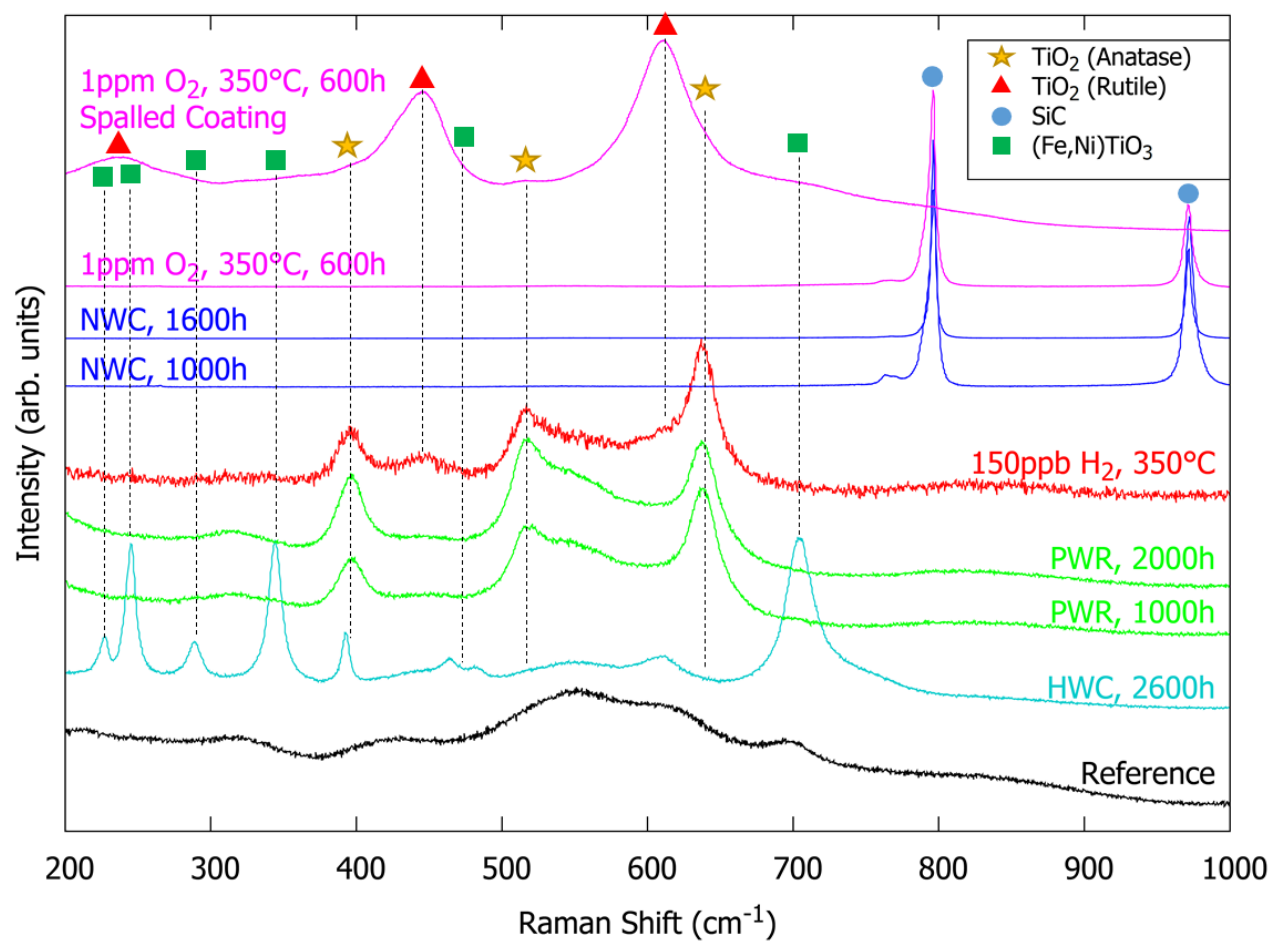


Figure 4.31: Raman spectra of TiN-coated samples exposed to various corrosion conditions, and as received. A 532 nm laser with a power of 1.6 mW was used to collect each spectrum. Exposure conditions and sampling locations are given on the graph with similar exposures plotted with the same color. Where not noted, a random location in the center of the sample was chosen.

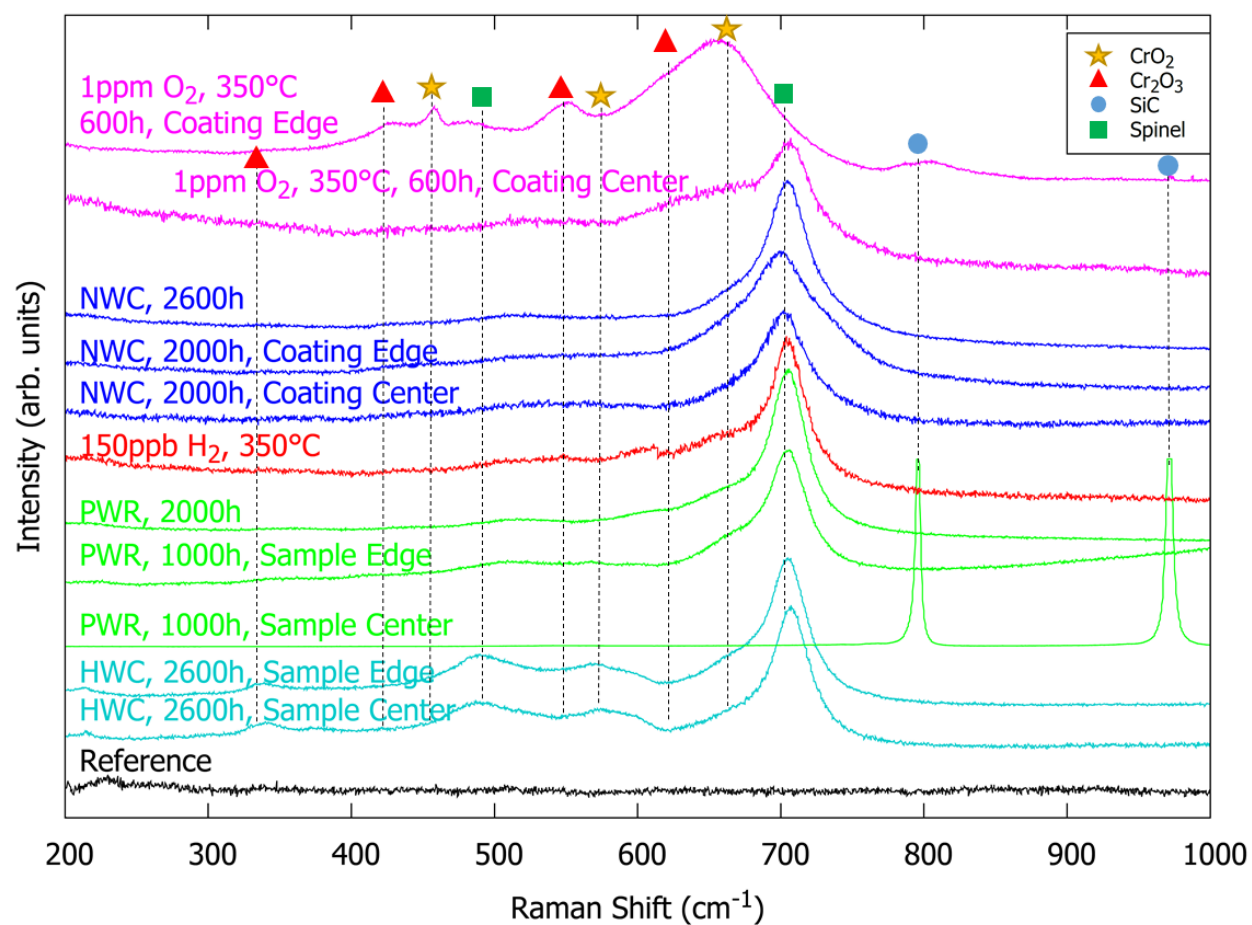


Figure 4.32: Raman spectra of monolithic CrN-coated samples exposed to various corrosion conditions, and as received. A 532 nm laser with a power of 1.6 mW was used to collect each spectrum. Exposure conditions and sampling locations are given on the graph with similar exposures plotted with the same color. Where not noted, a random location in the center of the sample was chosen.

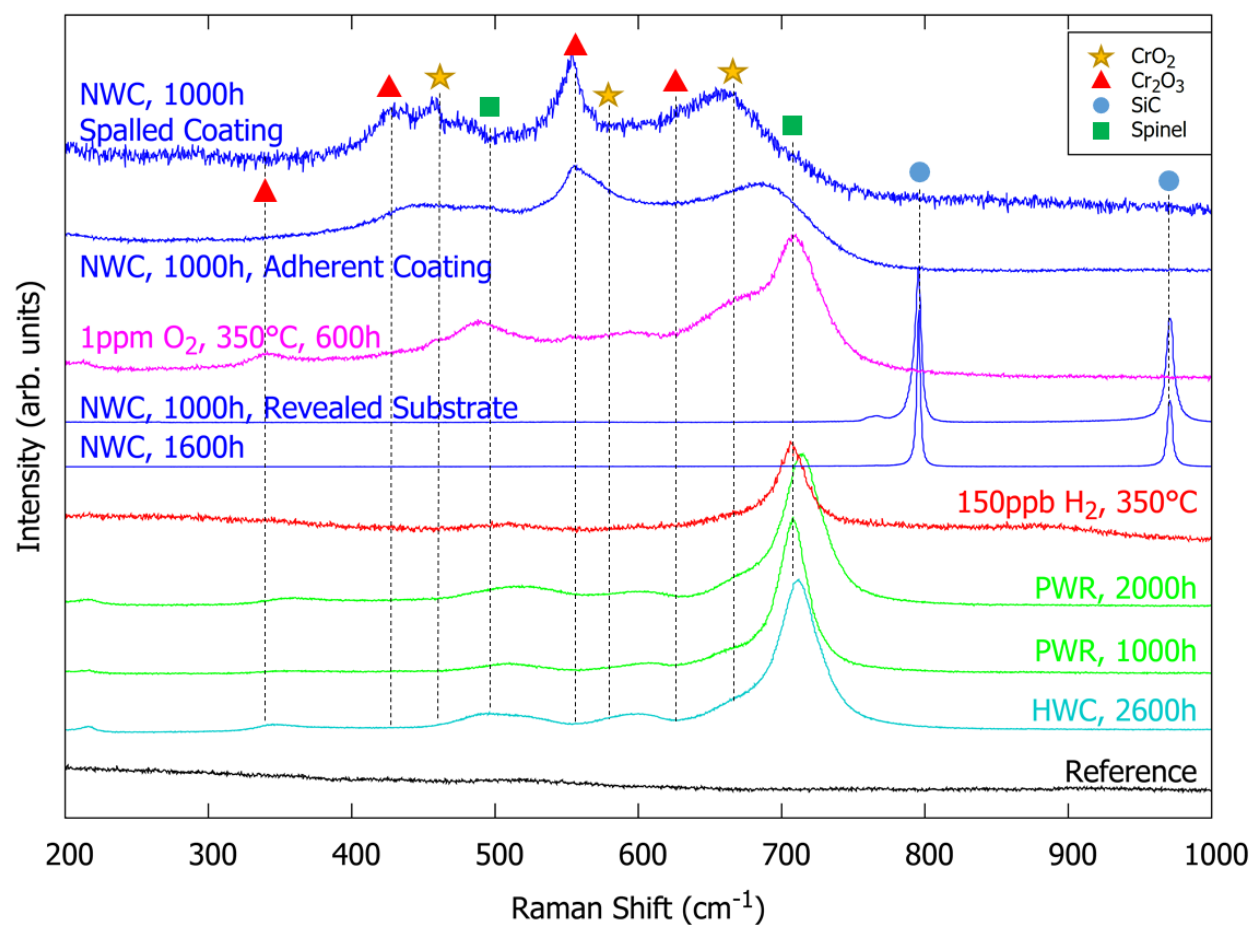


Figure 4.33: Raman spectra of Cr-coated samples exposed to various corrosion conditions, and as received. A 532 nm laser with a power of 1.6 mW was used to collect each spectrum. Exposure conditions and sampling locations are given on the graph with similar exposures plotted with the same color. Where not noted, a random location in the center of the sample was chosen.

observed and the coating is not (NWC). Second, at 1000h in NWC, both the adherent and spalled coating did not reveal any spinel and had a large concentration of the thermodynamically stable Cr_2O_3 .

4.4.4 Microscopy

SEM-BSE images and relevant EDS maps of the surface of as-exposed coatings are given in Figure 4.34-Figure 4.39. Cross-section images are presented in Figure 4.41-Figure 4.46. The multilayer Cr/CrN is not discussed in this section as it immediately spalled, Figure 4.28, and thus was either poorly adhered or simply spalled from thermal cycling. A variety of observations can be made from the data on the other three coatings.

TiN oxidized rapidly in oxygenated environments resulting in its entire consumption across most of the surface. Figure 4.34 presents several images showing only small oxide nodules remaining on the SiC surface where the TiN originally was, along with some continuous coating. The vast majority of the surface did not have any coating or oxide on it. This is further shown in cross-section, Figure 4.45. Moreover, the coating shown in Figure 4.45 was significantly or entirely oxidized and the oxide was not observed to be adhered to the substrate, but was attached to it via a small amount of unoxidized coating. Some small oxide particles were present on the surface without any unreacted substrate visible, Figure 4.45f, consistent with the surface observation of small nodules remaining.

In the absence of oxygen, the TiN coating was not broadly removed from the surface, but a few areas of localized spallation were observed, Figure 4.35. A variety of macroparticles were found on the surface, some reaching to the SiC/TiN interface and others reaching less deep. The interface between macroparticles and the surrounding coatings became oxidized with exposure, as in Figure 4.46. Interfacial oxidation of the coating was also observed and linked to cracking of the coating normal to the interface, Figure 4.46 c, and e.

Cr, likewise, oxidized rapidly in the presence of oxygen and was largely removed, Figure 4.38a, leaving scattered oxide particles behind on the surface. A net recession of the coating to less than 3 μm , depending on the region, was observed after NWC exposure and this is depicted in Figure 4.40a and b. Localized spallation, Figure 4.38b, was also observed and is particularly initiated near edges or engraving marks, which act as stress concentrators. Where the coating was adherent it was covered with a large number of oxide crystallites. In cross-section of the 1ppm O_2 exposure at 350°C, Figure 4.42, these crystallites covered a large number of pit-like features which extended nearly to the interface. In some cases oxidation of the interface was observed and could be linked to through-cracks in the coating. This behavior was not observed in deoxygenated environments. No significant oxidation or recession of the coating was observed. Localized spallation did still occur at 350°C but was not apparent in the HWC environment.

CrN was observed to oxidize more slowly than either TiN or Cr in the presence of oxygen. The edges of the coating oxidized more quickly than the center, yielding a large number of oxide crystals, Figure 4.36. Away from the edges, the oxide crystals did not cover the surface, but were still visible. In cross-section, the bulk of the coating was observed to be entirely intact with no easily observable oxide on the coating surface. Near the edge, however, the coating was

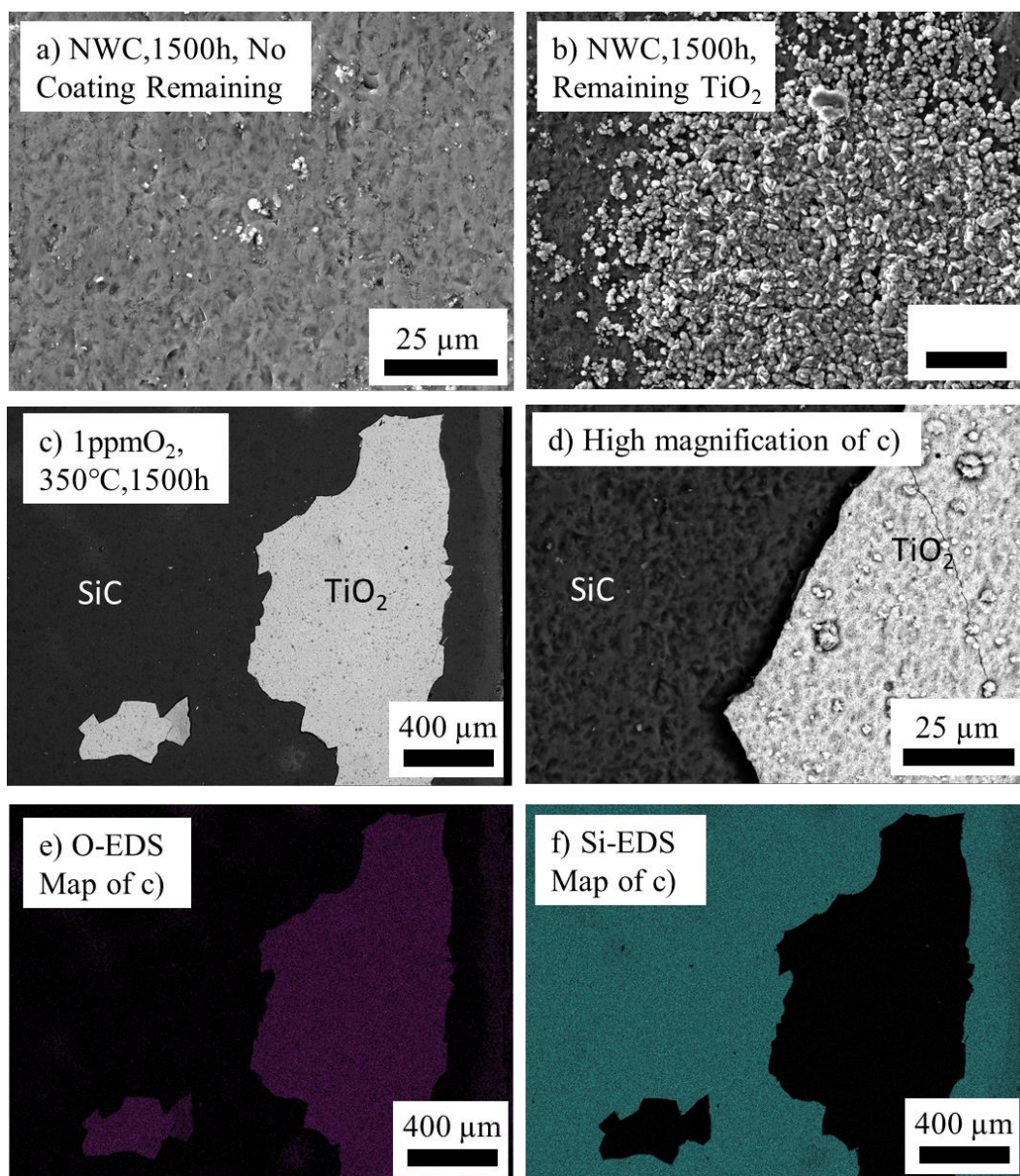


Figure 4.34: SEM-BSE images of TiN-coated SiC exposed to oxygenated conditions. a) and b) represent the NWC exposure for 1500h on a nearly bare portion of the sample, a), and a region with substantial oxide remnants, b). c) shows the BSE image of the sample exposed to 350°C and 1 ppm O_2 for 600 hours. e) and f) show O and Si EDS maps, respectively, of the region in c), revealing both the coating and substrate, as labeled in c). A higher magnification image of the region in c) is provided in d).

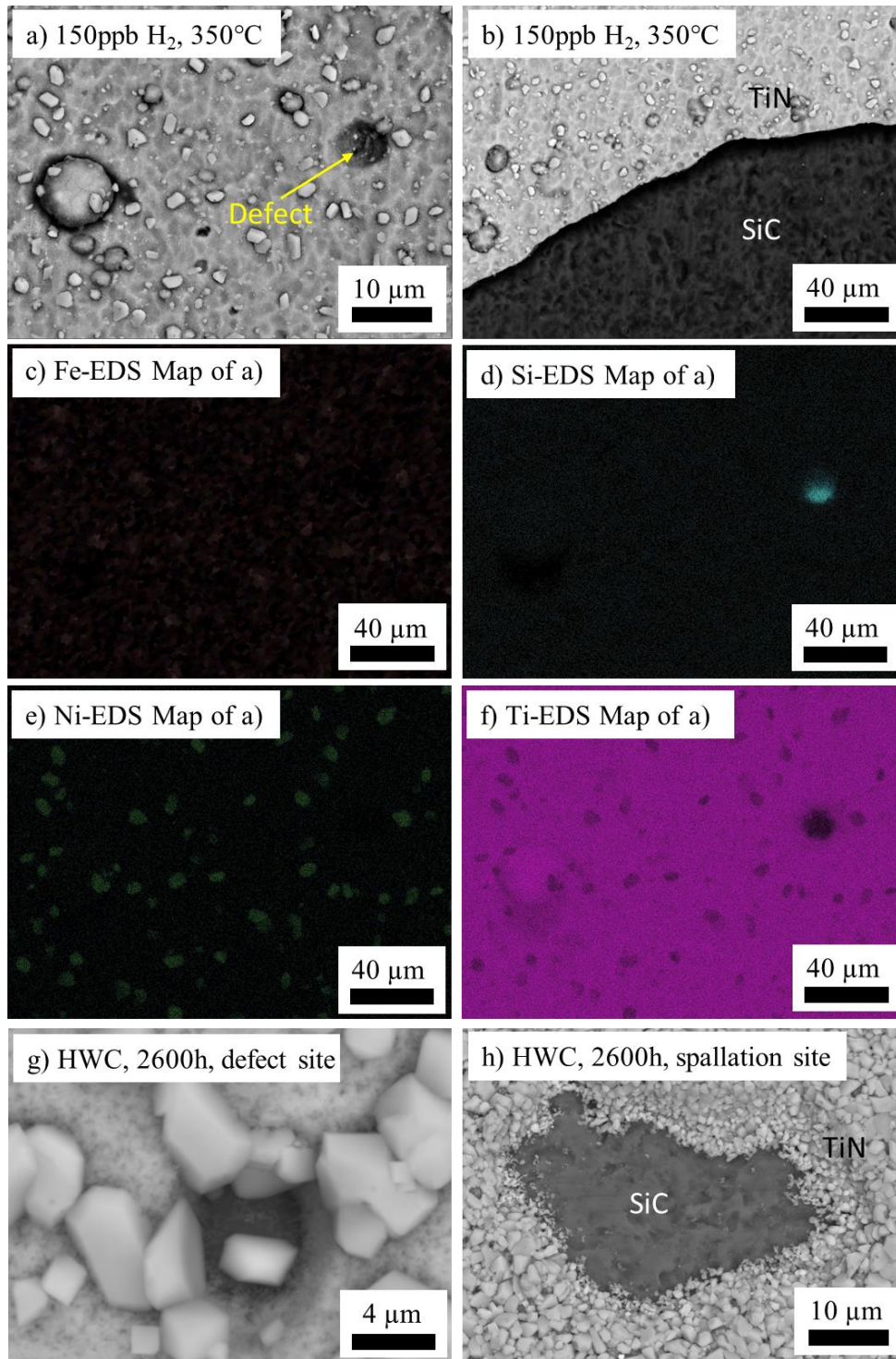


Figure 4.35: SEM-BSE images of TiN-coated SiC exposed to deoxygenated conditions. The sample exposed at 350°C are provided in figures a)-f). a) shows a mostly intact coating surface with a small defect, as labeled. Fe, Si, Ni, and Ti EDS maps of the region are given in c), d), e), and f), respectively. b) represents the interface between an intact portion of the coating and a spalled region. Two defect regions resulting from exposure to the HWC environment for 2600 hours are shown in g) and h).

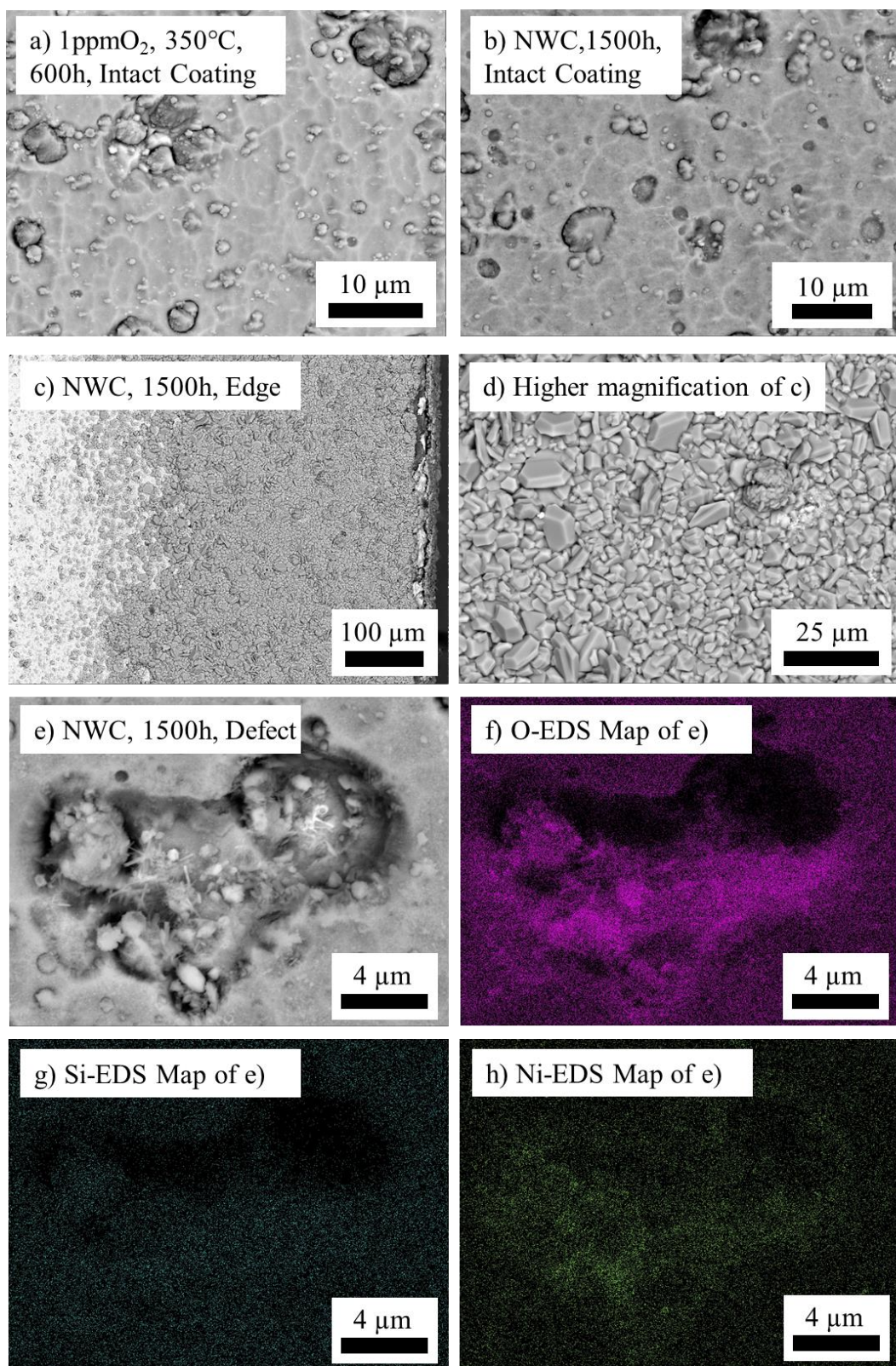


Figure 4.36: SEM-BSE images of CrN-coated SiC exposed to a) 1ppm O₂ at 350°C for 600 hours, and b)-h) NWC for 1500 hours. Intact coating far from the edge is shown in a), b), and e)-h). The edge of the coating is shown in c) and d) with substantial oxide buildup. EDS maps of O, Si, and Ni across a defect in the coating are shown for f)-h).

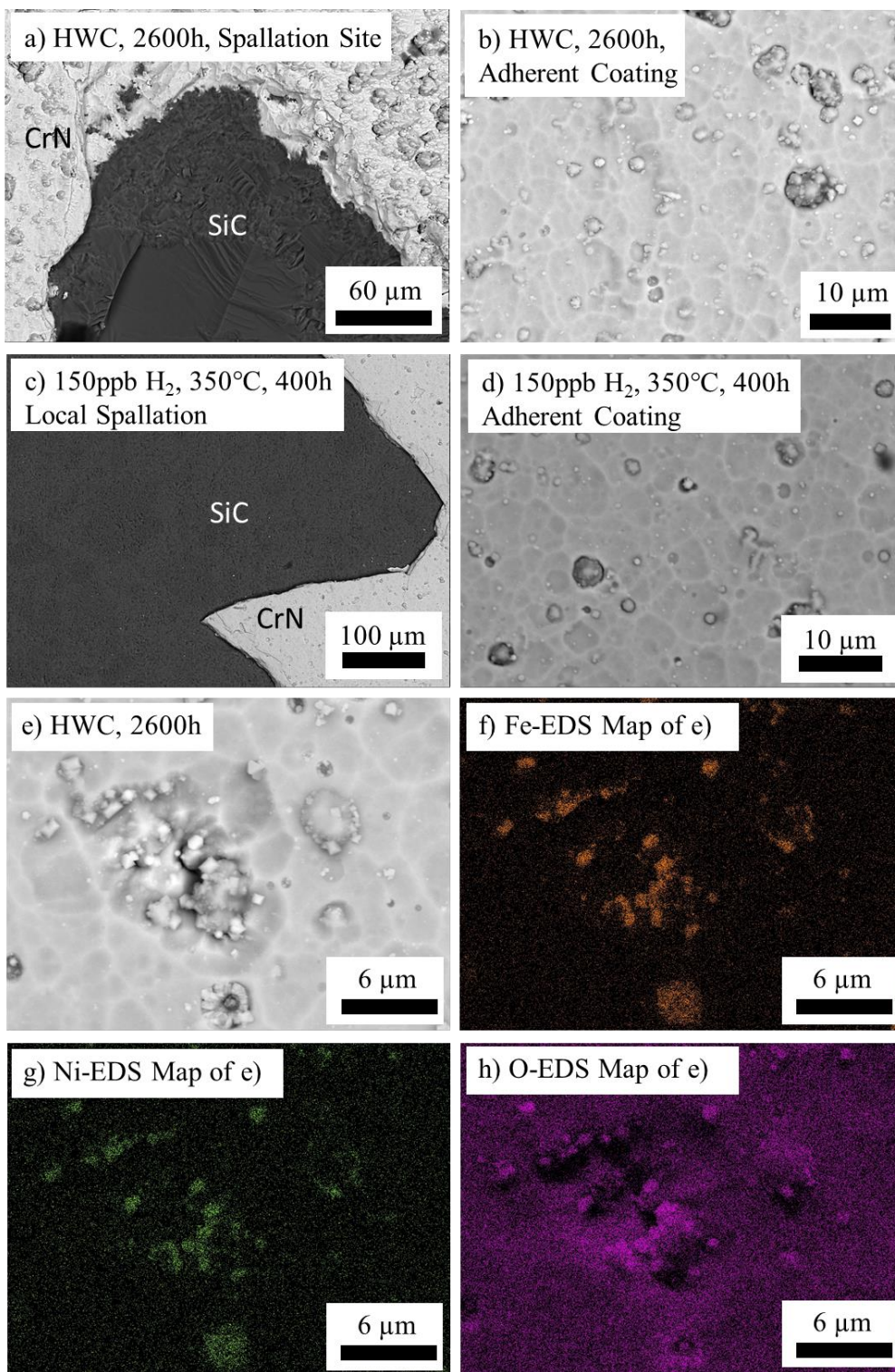


Figure 4.37: SEM-BSE images of CrN-coated SiC exposed to HWC for 2600h, a), and b), and to 350°C with 150ppb H_2 for 400h, c) and d). Both well adhered coating, b) and d), and partially spalled coating, a) and c), are given. Oxide formation on the HWC-exposed sample is shown in e)-h) with Fe, Ni, and O EDS maps.

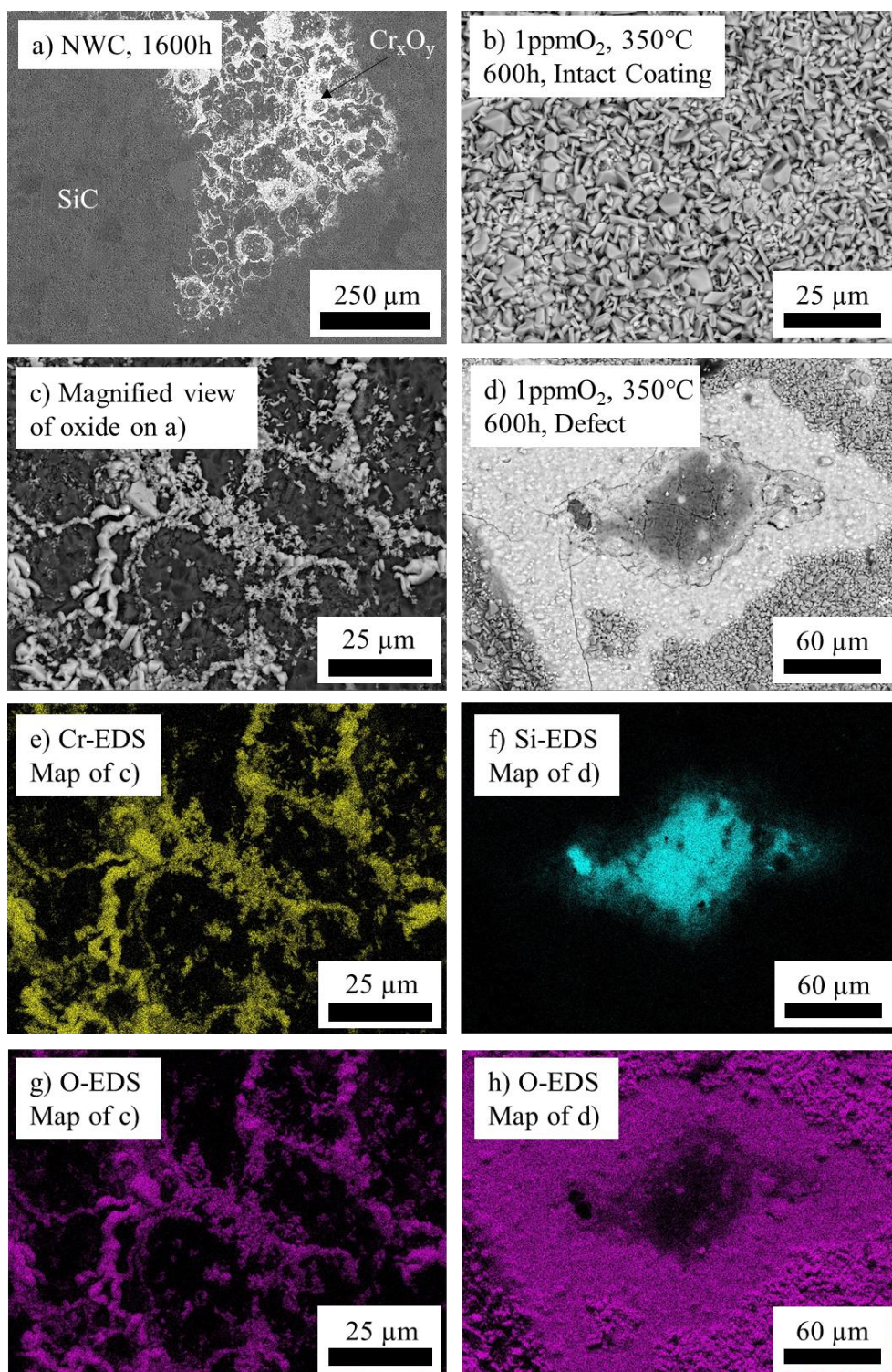


Figure 4.38: SEM-BSE images of Cr-coated SiC exposed to NWC for 1600 hours a), c) e), and g) and 350°C with 1ppm O_2 for 600 hours, b), d), f), and h). Cr and O EDS maps of the oxide particles in image c) are given in e) and g), respectively. Si and O EDS maps are given in f) and h) to confirm the partial spallation shown in d).

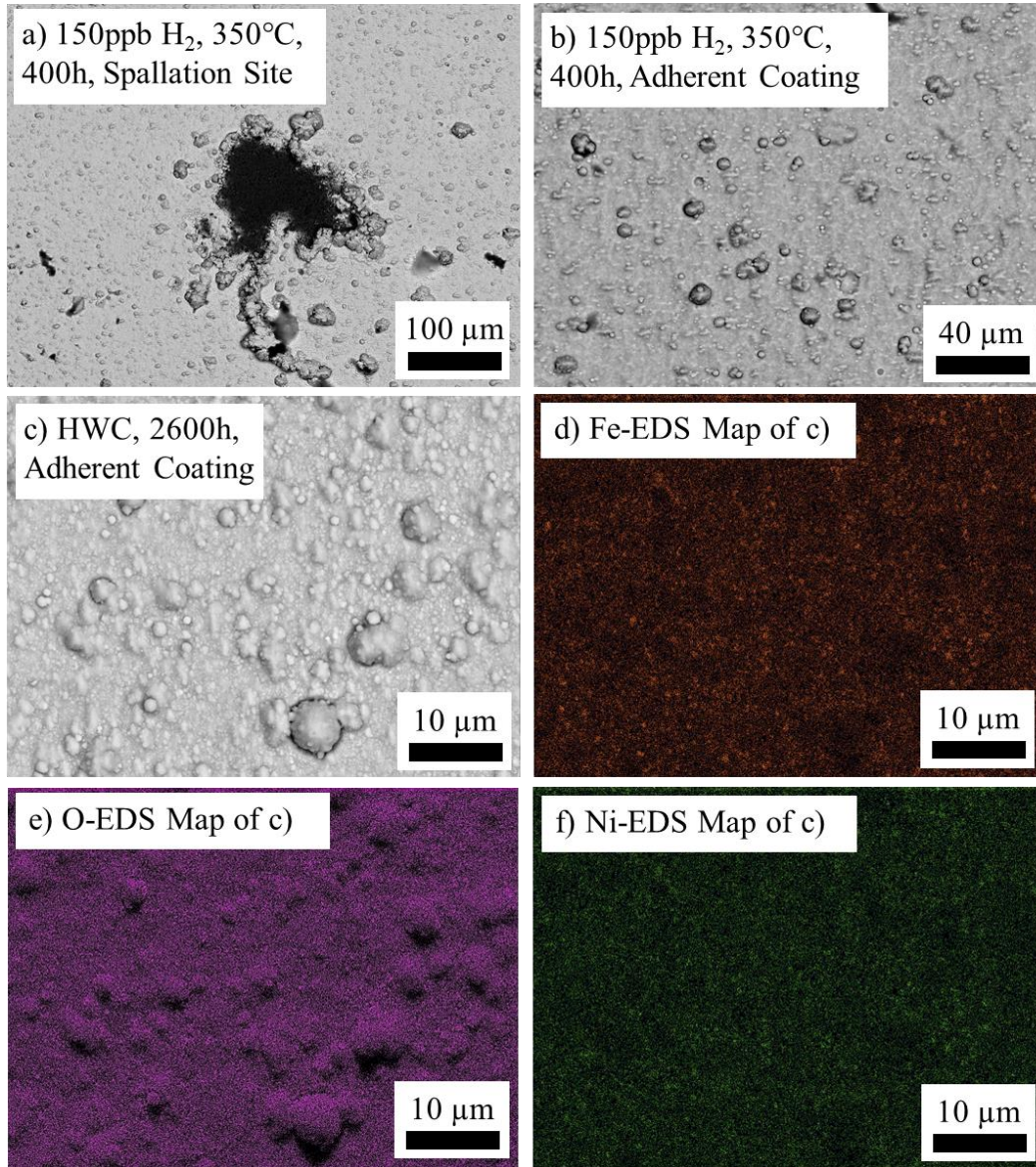


Figure 4.39: SEM-BSE images of Cr-coated SiC exposed to deoxygenated conditions. a) shows localized spallation of the coating exposed to 150ppbH₂ and 350°C for 400h while b) presents an adhered region of the coating at higher magnification. A representative micrograph of the surface after 2600 hours of exposure to the HWC environment is given in c). EDS maps of Fe, Ni and O show small oxide particles on the surface of c).

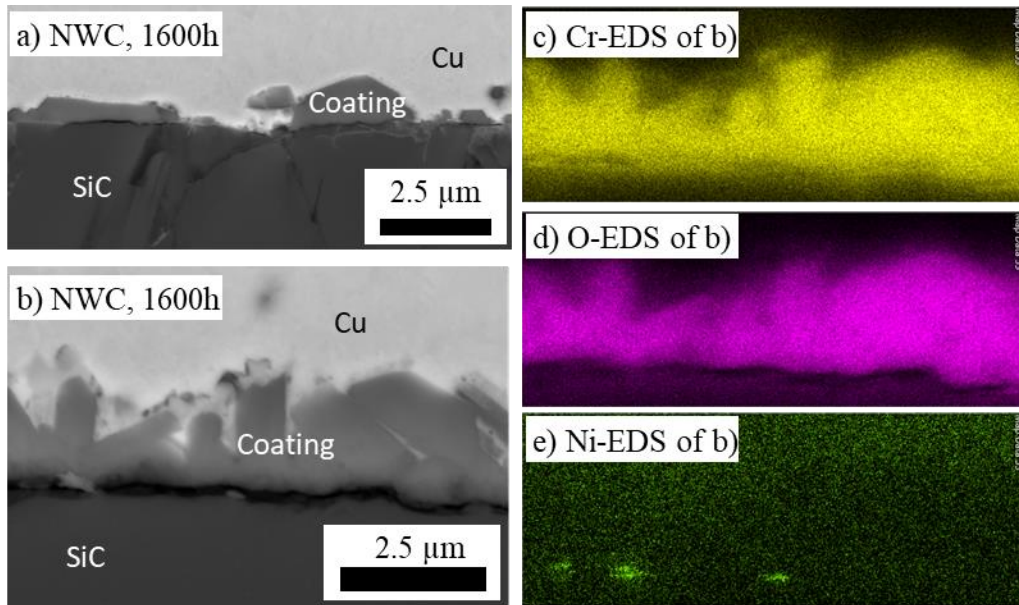


Figure 4.40: SEM-BSE images of cross-sectioned Cr-coated SiC exposed to NWC conditions for 1600 hours. a) and b) show two different regions of the coating cross-section. c), d), and e) show Cr, O, and Ni EDS maps of the region in b).

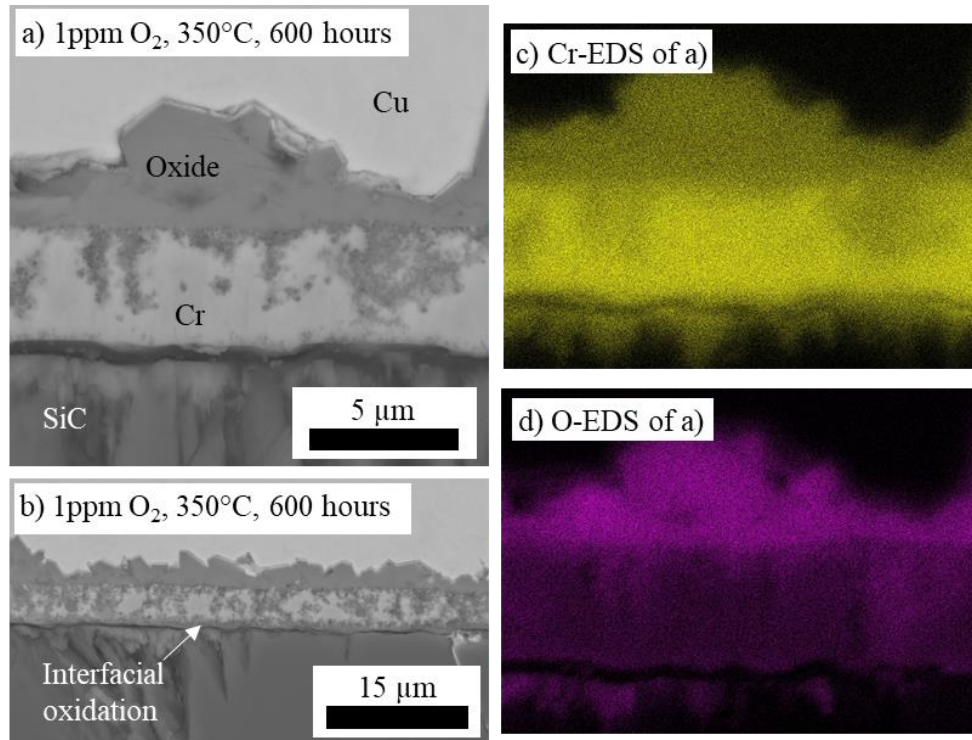


Figure 4.41: SEM-BSE images of cross-sectioned Cr-coated SiC exposed to 350°C water with 1ppm O₂ for 600 hours. a) shows a high magnification image. c) and d) show EDS maps of Cr and O for image a). b) shows a separate region with interfacial oxidation.

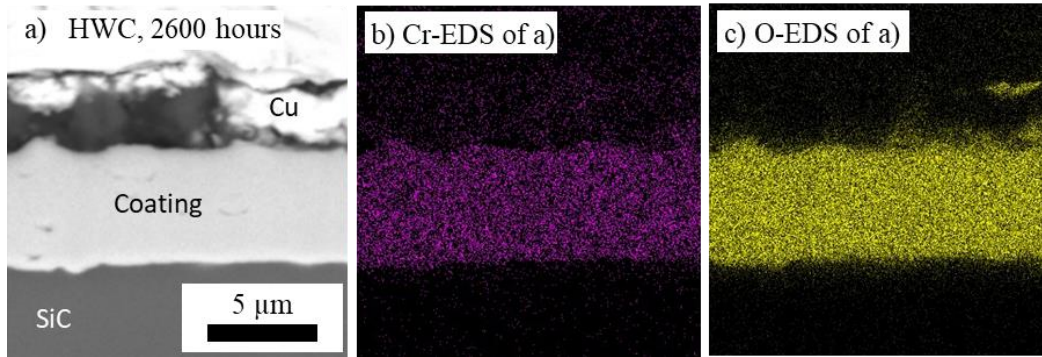


Figure 4.42: a) SEM-BSE image of cross-sectioned Cr-coated SiC exposed to HWC conditions for 2600 hours. b) and c) show Cr and O EDS maps of the region in a).

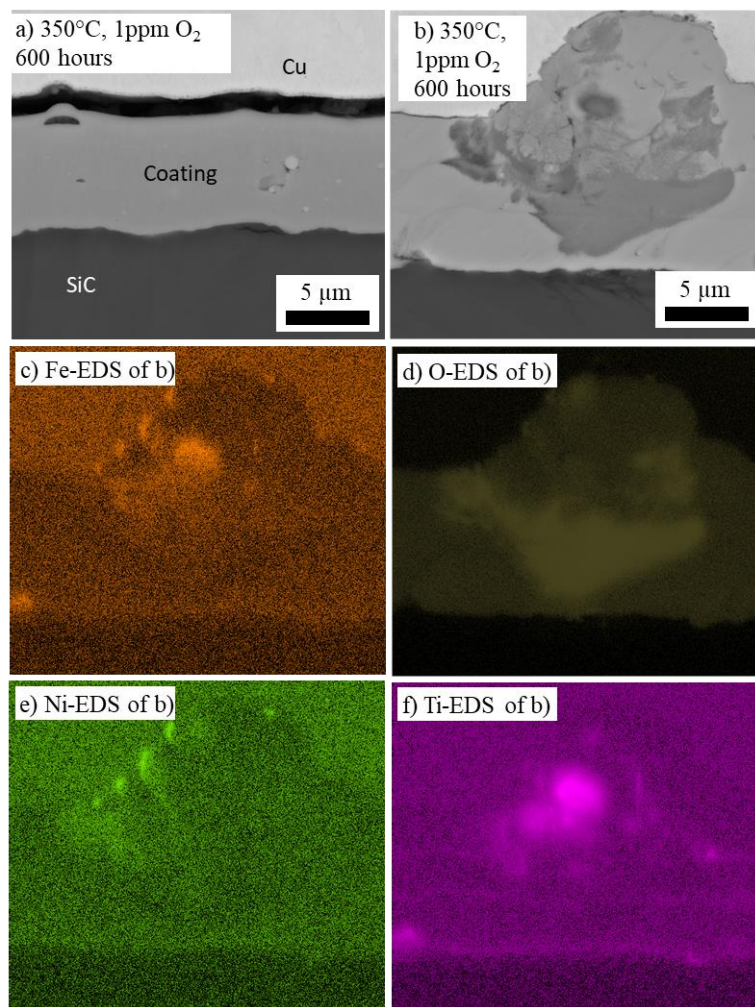


Figure 4.43: Cross-section images of CrN-coated SiC exposed to 350°C water with 1ppm O_2 for 600 hours. a) and b) show two SEM-BSE images without large defects and with a large defect, respectively. c)-f) show Fe, O, Ni, and Ti EDS maps of the region in b) revealing Ti metal particles.

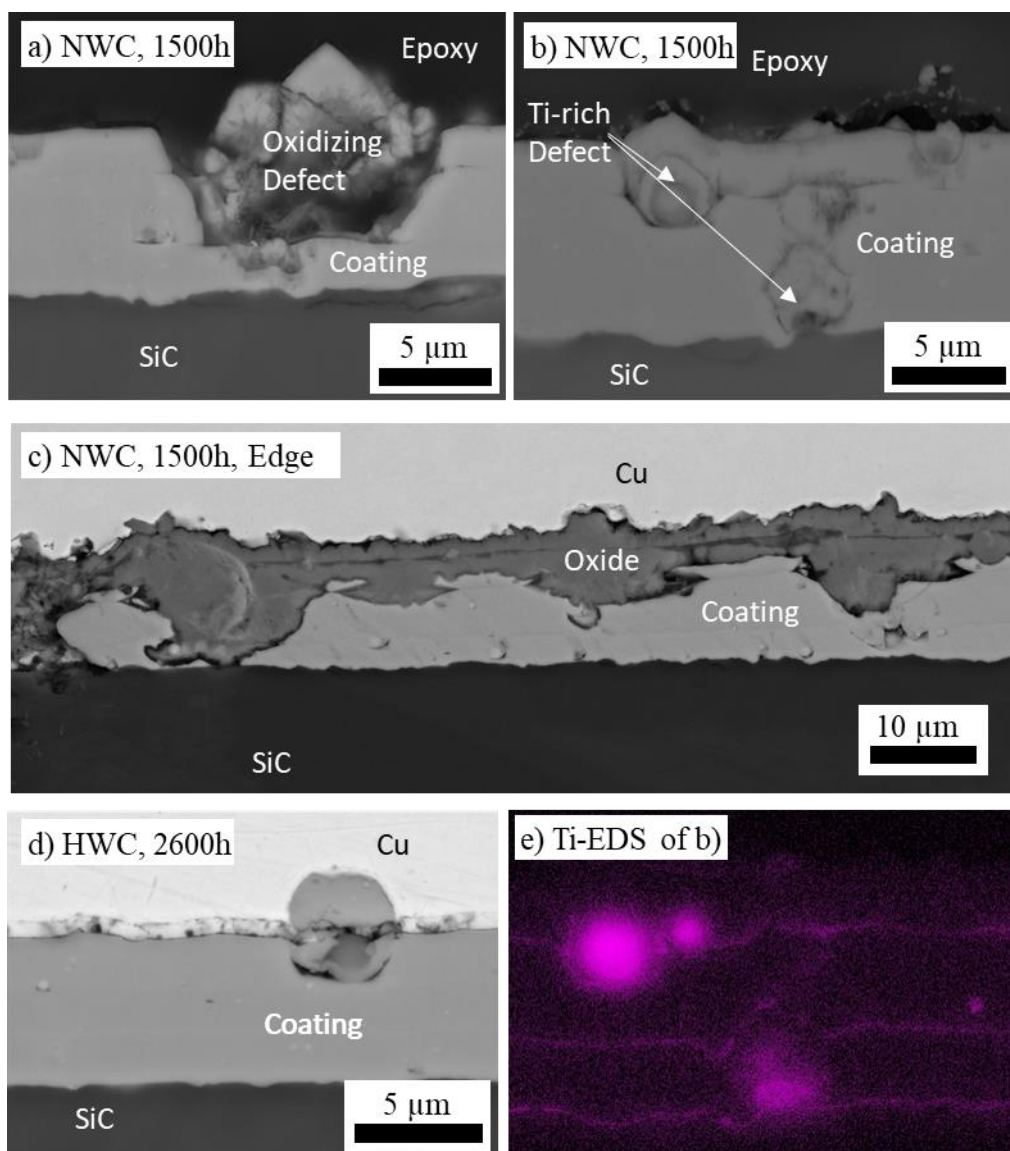


Figure 4.44: SEM-BSE images of defects in CrN-coated SiC exposed to NWC conditions for 1500h a) and b) with a Ti EDS Map of the b) region given in e). The coating near the edge is shown in c) with significant oxidation. A similar micrograph of the coating exposed to the HWC environment for 2600h is given in d).

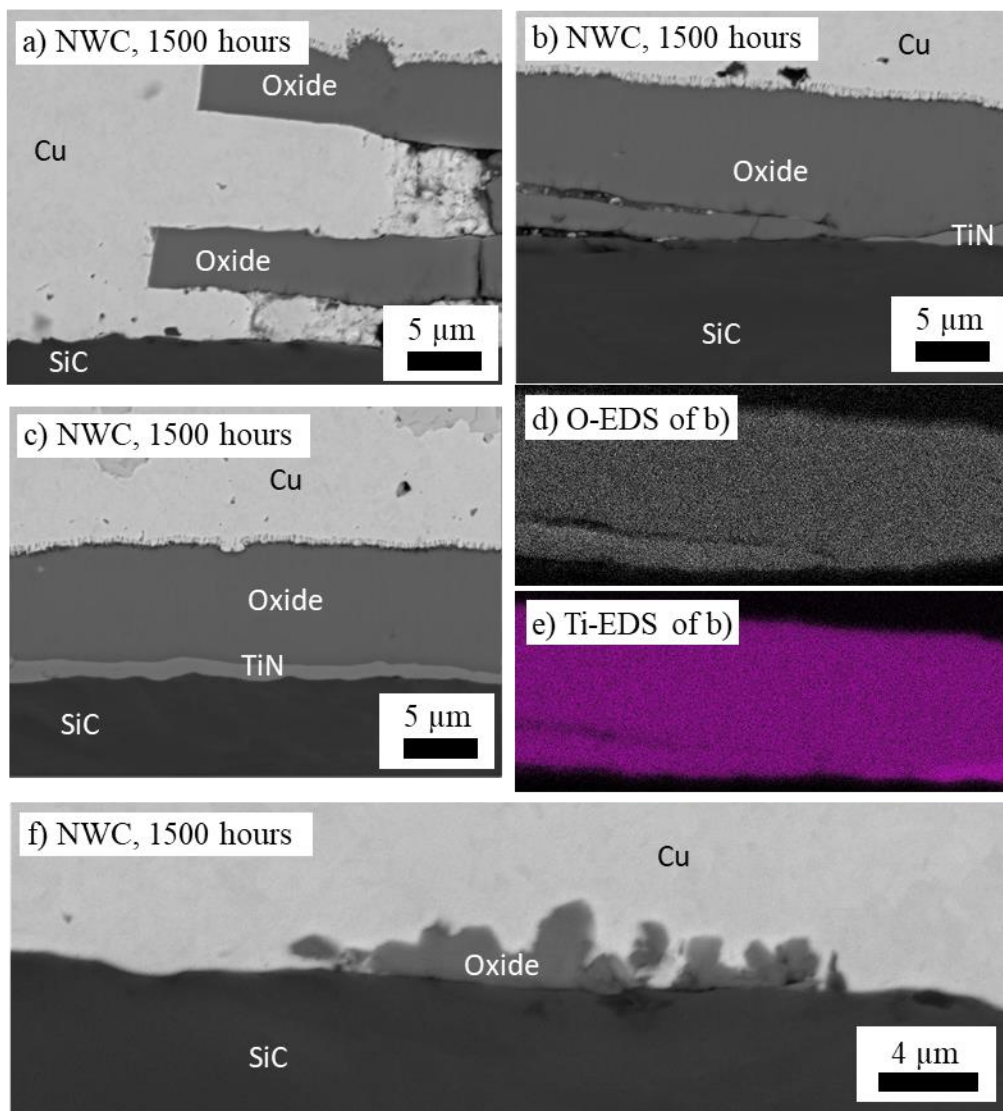


Figure 4.45: SEM-BSE images of TiN exposed to NWC conditions for 1500h. a) shows a completely oxidized coating with an attachment point to the SiC substrate shown in b). A fully adhered coating with oxide is shown in c). The vast majority of the sample did not contain any oxide at all. c) and d) show the EDS maps of O and Ti, respectively for image b). Small amounts of adhered oxide on the SiC surface are shown in f).

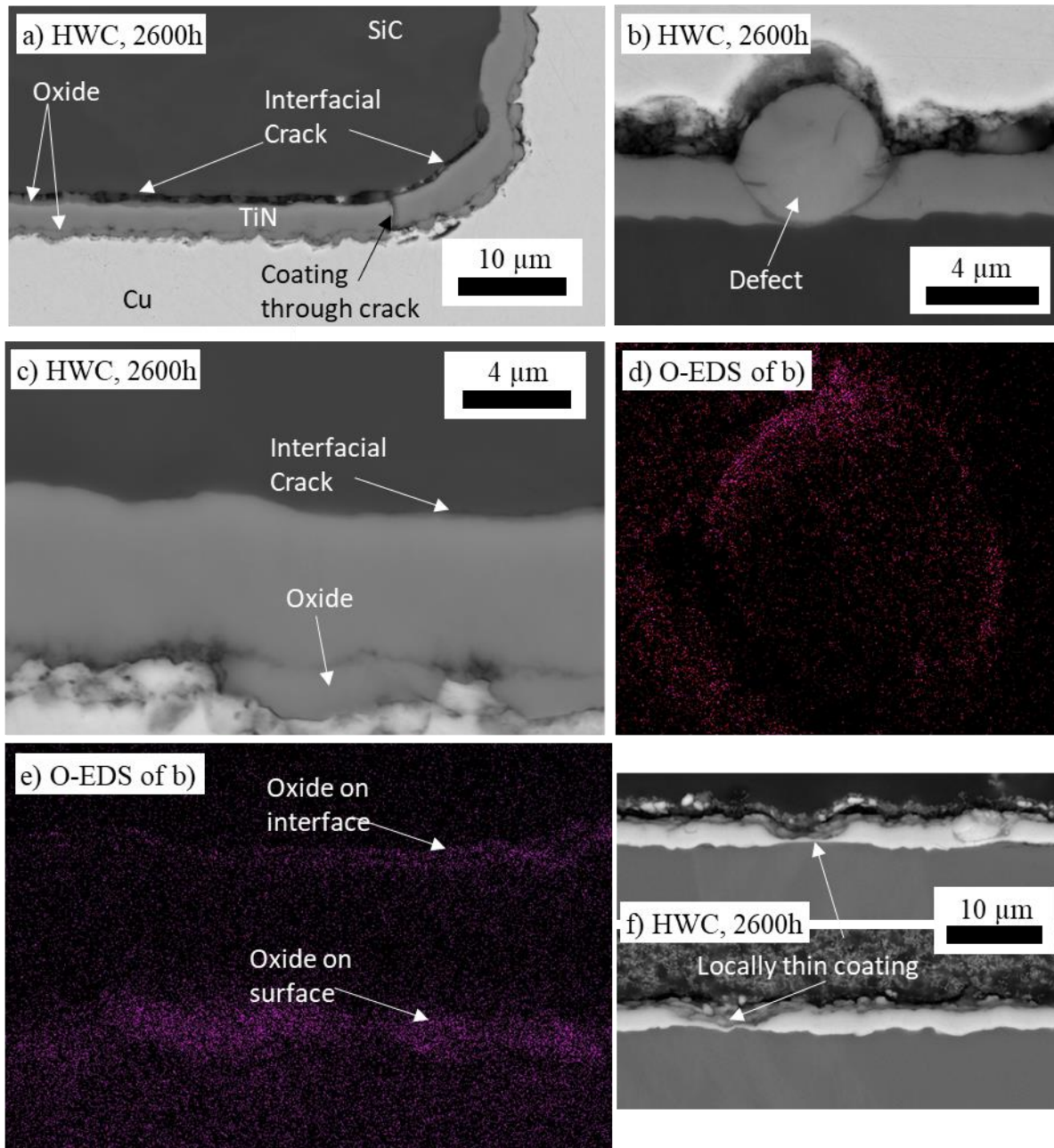


Figure 4.46: SEM-BSE images of TiN exposed to HWC water for 2600 hours. a) and b) show coating defects. Most of the coating was well-adhered, as in f), with a variety of as-deposited defects such as in b). c) gives a high magnification image of the coating at the crack termination point, near a), and e) proves the corresponding oxygen EDS map. Similarly, d) shows the oxygen map surrounding the particle defect in b).

significantly oxidized and even reached the SiC/Coating interface at a few points, Figure 4.44.

In addition, some localized spallation was observed and EDS evaluation showed that many macroparticles were composed of Ti metal which was present on the interface as a compatibility coating. As shown in Figure 4.44d, 3-4 Ti interlayers were placed uniformly throughout the coating and the Ti particles were thus also dispersed across the coating. Figure 4.43 and Figure 4.44 show that these macroparticles are the onsets both of significantly enhanced oxidation and can be crack initiation sites, with cracks occasionally propagating through a Ti interlayer.

4.5 MITR Exposures of Coated SiC

4.5.1 Behavior of Coatings Under Irradiation in Ar

XRD was used to examine phase changes and swelling of the lattice by point defects.

Representative plots of diffraction data from 30 to 90 degrees 2θ are given in Figure 4.47. The black lines indicate the as-received sample, and the red lines indicate the same sample following irradiation. In thick coatings (such as monolithic Cr and multilayer Cr/CrN) no SiC peaks were detectable, whereas the thinner coatings (monolithic CrN, and TiN) at least a few of the SiC peaks become visible. Following alignment of Si standard peaks, small downward shifts of each visible SiC peak were observed, consistent with the expected point-defect swelling of SiC expected under LWR irradiations. Coating peaks lined up identically, or nearly so with the pre-irradiation scans. This data is further evaluated in the Discussion section.

Figure 4.48 shows the radiation-induced change in lattice parameter in each of the exposed samples in the dry irradiation environment. The lattice parameter changes were determined using Rietveld refinement to fit the as-received XRD and the post-irradiation spectra and comparing the resulting lattice parameters. Error bars were obtained from the standard deviation of the lattice parameter shift. Both high and low resistivity SiC swelled at comparable rates, equivalent to approximately 1.7% volumetric swelling, typically observed to be due to point defect saturation below the onset of significant vacancy mobility [21]. No significant changes in the lattice parameter of the three coating materials was observed, with measured irradiated values within 0.02% of the unirradiated values. The potential exception is the monolithic CrN, which appeared to slightly densify.

Representative optical micrographs of the samples after irradiation in Ar are presented in Figure 4.49. Cracking was not observed in the TiN samples. Small, sparsely populated cracks were observed in the monolithic CrN samples, as shown in Figure 4.49, additional images are given in Appendix B. Cracks in the multilayer CrN/Cr and Cr samples were numerous and appeared to be more open. These cracks were not observed on as-received coating samples. A summary of the coating cracking measurements is presented in Figure 4.49. The crack densities in Figure 4.50 were obtained by measuring the total line length of cracks in several optical surface images and dividing by the image total area. Cracks were not observed in the TiN coatings and some cracking was observed in the monolithic CrN. Both the Cr and multilayer Cr/CrN coatings cracked significantly with no dependence on SiC substrate type.

Cross-sectioning of the samples followed by SEM examination allowed examination of the extent of cracking (e.g., through-cracking versus partial cracking of the coating). Representative

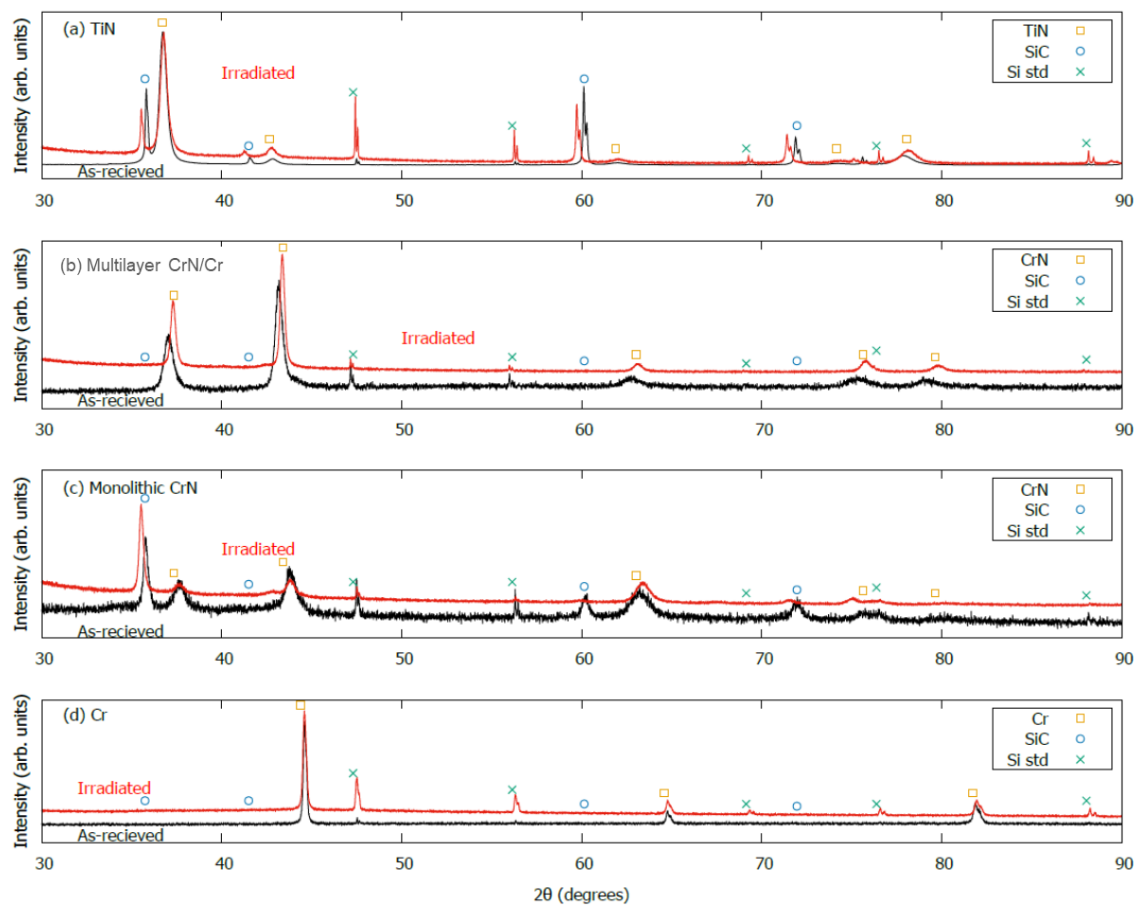


Figure 4.47: X-ray diffraction patterns for representative samples under MITR dry irradiation in Ar to about ~0.5 dpa. All subplots show comparison of irradiated and unirradiated samples. a) monolithic TiN, b) multilayer Cr/CrN, c) monolithic CrN, and d) monolithic Cr.

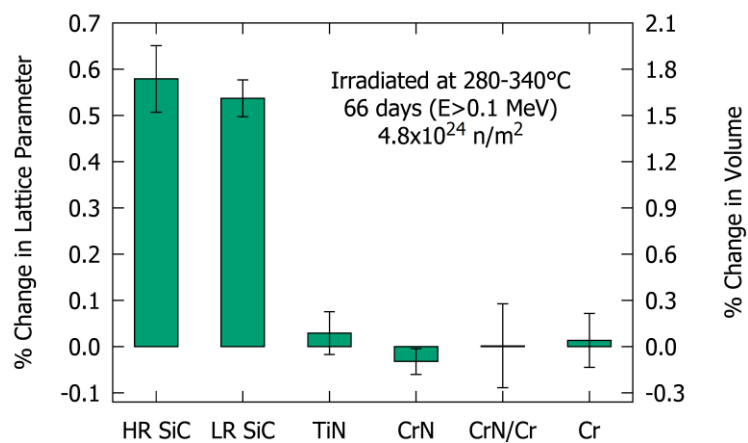


Figure 4.48: Lattice swelling of material types exposed to MITR dry irradiation to about 0.5 dpa.

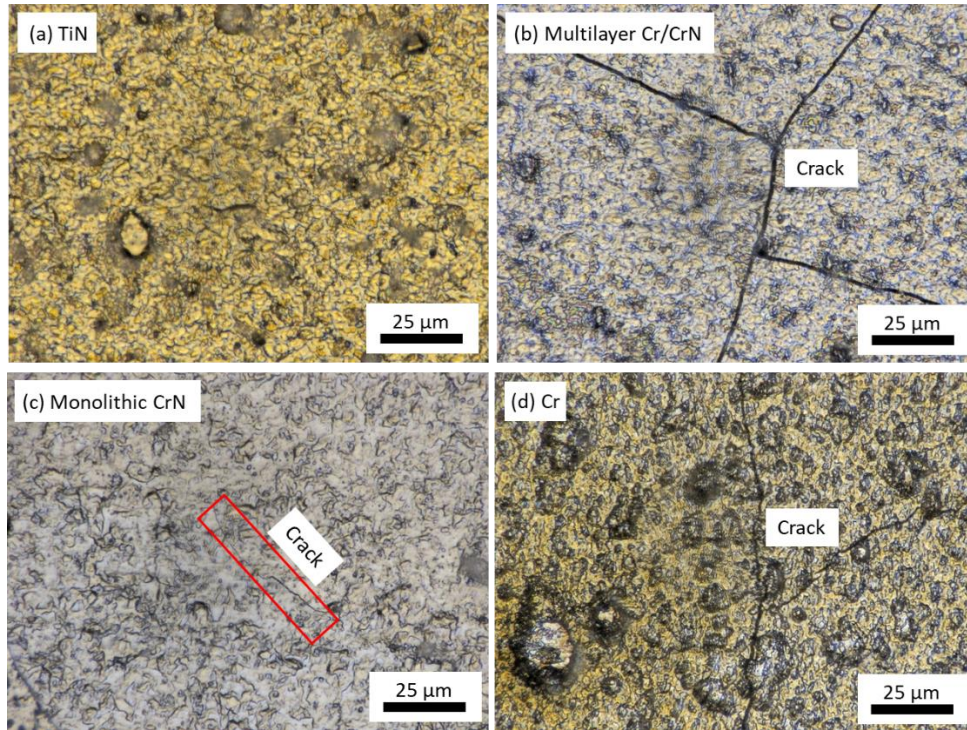


Figure 4.49: Representative optical micrographs demonstrating cracking in MITR dry-irradiated coating materials. a) monolithic TiN, b) monolithic CrN, c) multilayer Cr/CrN, and d) monolithic Cr.

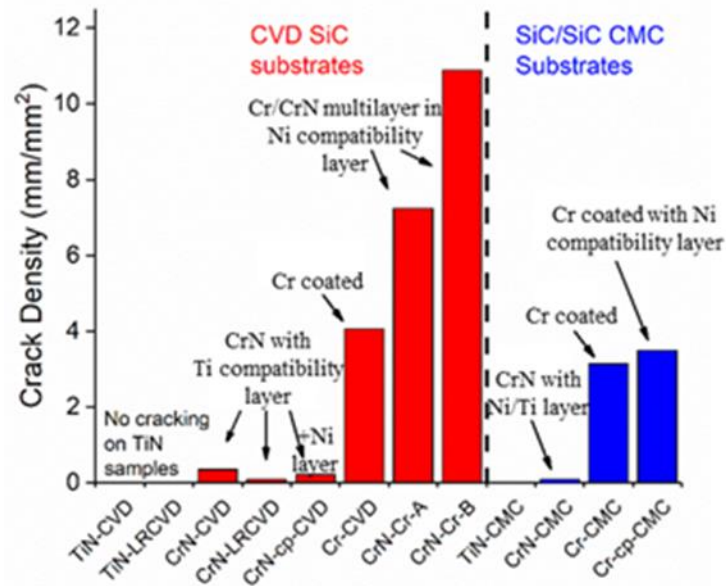


Figure 4.50: Surface cracking density of samples exposed to MITR dry irradiation environment in Ar to a damage of about 0.5 dpa. From [108].

micrographs are presented in Figure 4.51. Several observations can be made from this figure.

First, some localized cracks or coating defects were observed in the TiN-coated SiC. However, all observed cracks were linked to underlying crack networks or defects in the SiC which propagated to the surface and thus through the coating. This is similar to the reference specimens (not shown) where the coatings were intact for all coating systems, except for where such cracks appeared linked to underlying SiC defects. An example is shown inset to Figure 4.51a. Second, in the multilayer CrN/Cr samples all cracks reaching the coating surface appeared to originate at the interface, as shown in the figure. No deflection of cracks by the multiple Cr interlayers was observed. Additionally, some partial cracks (example shown by inset in Figure 4.51b) were observed to propagate from the surface half-way through the coating. As shown, the partial cracks passed through several inter-layers prior to terminating near an interlayer. Cracking along the SiC/CrN interface was not observed. Third, all cracks normal to the interface in the monolithic CrN and Cr coatings propagated entirely through the coating (shown by inset in Figure 4.51c). However, unlike the Cr/CrN coating, the interface of both coatings was significantly cracked. About 60% of the observed cross-section was cracked and over half of the remaining interface was clearly crumbled (see inset in Figure 4.51d). Approximately 20% of the interface of the monolithic CrN was cracked.

Following cross-section evaluation in the SEM, FIB liftouts were examined by TEM to identify microstructure-related defects that may explain the observed cracking. Near the middle of the coating, the focus/defocus technique was used to identify any voids. The results are shown in Figure 4.52. No voids were observed for TiN or CrN (Figure 4.52a, b, d, and e). However, the Cr micrographs (Figure 4.52c and f) reveal a uniform distribution of small cavities in the irradiated specimen that were not seen in the unirradiated Cr specimen. The average diameter and number density of the voids were 2 nm and $1.5 \times 10^{23} \text{ m}^{-3}$, respectively, which corresponds to 0.2% void swelling ($\sim 0.07\%$ length change).

Examination of the coatings with TEM-EDS did not reveal any defect precipitation or phase transformation, as shown by Figure 4.53 for a Cr coating on R&H SiC. Similarly no second phase formation or solute segregation was observed in the other coating systems.

Transmission Kikuchi Diffraction (TKD) was also performed to understand the coating microstructure and is shown in Figure 4.54. A red line in Figure 4.54 denotes the Cr/SiC interface. While the SiC has large grains, as expected, the coating is made up of two regions. The first is the near-interface region, which is characterized by numerous small columnar grains around 100 nm in diameter. Around 1 μm away from the interface, the Cr grains become significantly larger, but are still primarily columnar, and exhibiting growth normal to the interface.

4.5.2 Effects of Radiation in PWR Water

Mass change data from the samples exposed to recirculating water in, above, and out-of the core is reported in Figure 4.55 and Figure 4.56. The secondary axis is a simple conversion to approximate thickness change. It was calculated by scaling the mass change by the density of the coating, assuming the surface area is represented well by a geometric area calculation. Localized

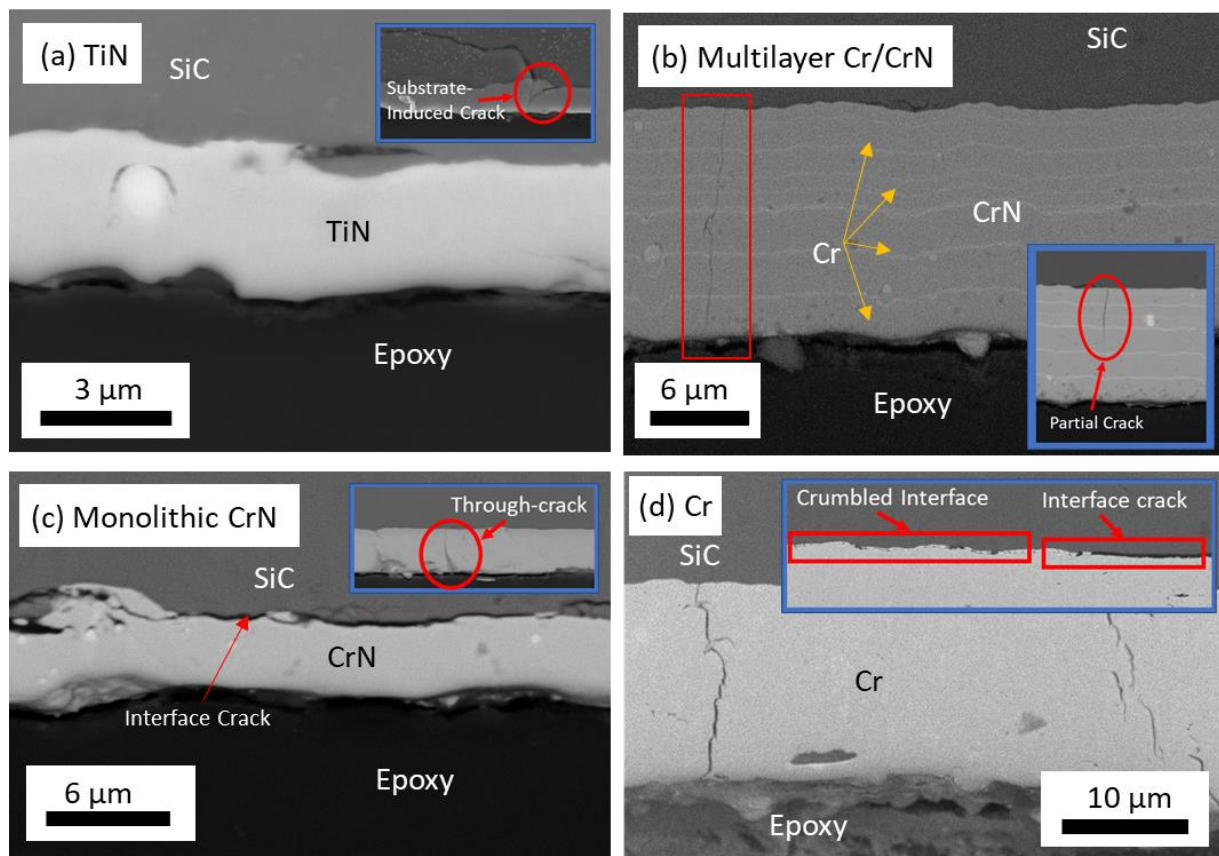


Figure 4.51: Scanning electron micrographs of coating systems exposed to MITR irradiation in Ar to a damage of about 0.5 dpa. a) monolithic TiN, b) multilayer Cr/CrN, c) monolithic CrN, d) monolithic Cr.

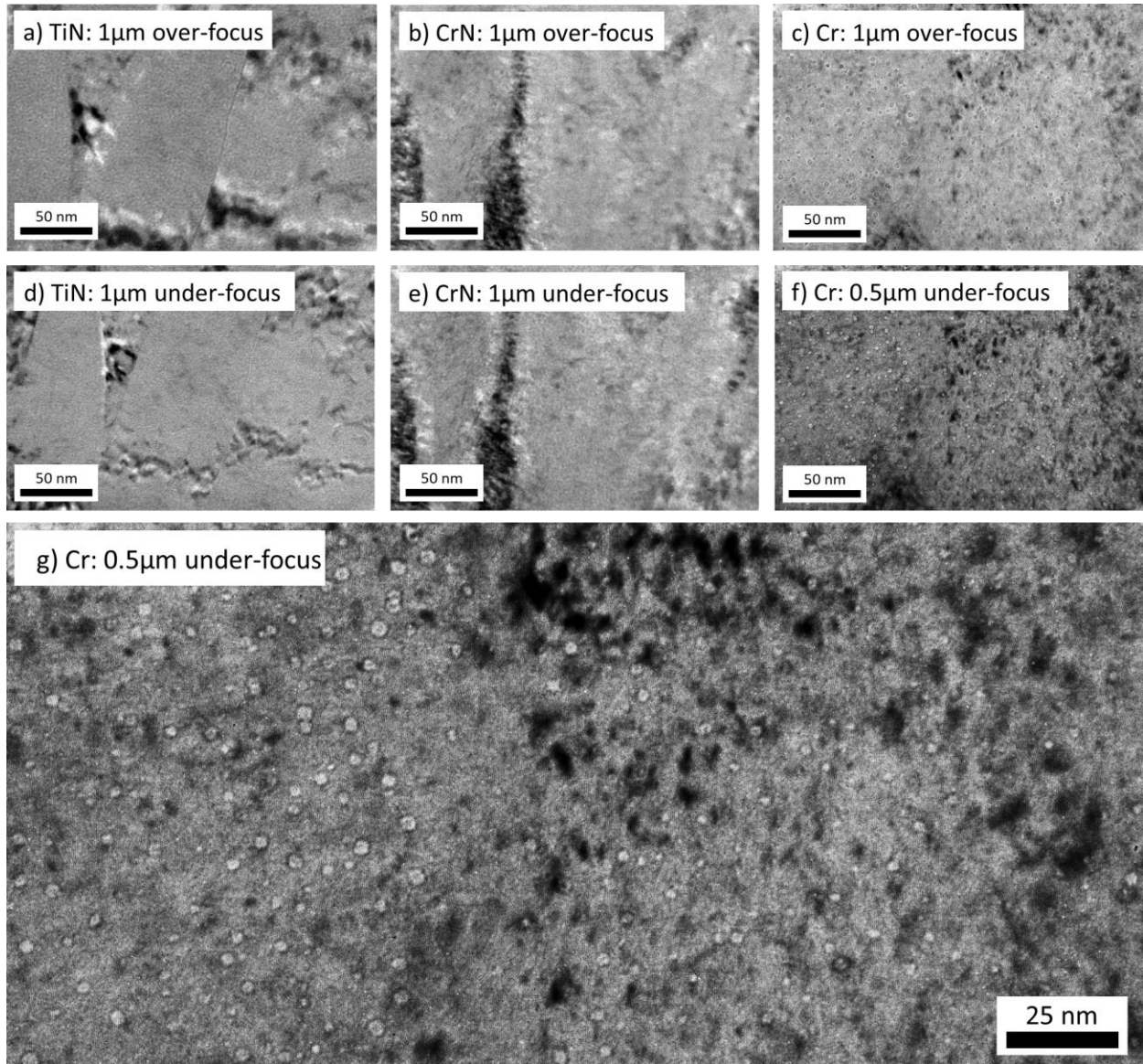


Figure 4.52: Transmission electron micrographs of a) and d) monolithic TiN, b) and e) monolithic CrN, and c) and f) monolithic Cr exposed to MITR irradiation in an Ar environment to a damage of about 0.5 NRT dpa. a), b), and c) correspond to a focused beam and d), e), and f) correspond to an under-focused beam showing voids in the Cr sample. g) is an expanded image of f) to more clearly show the void formation in Cr.

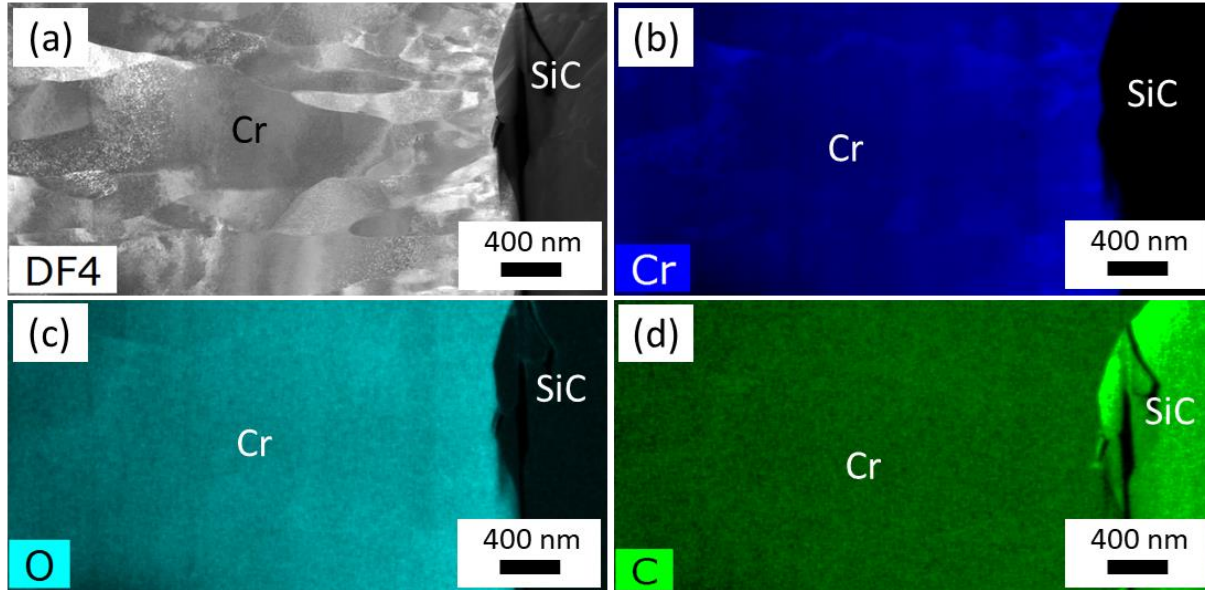


Figure 4.53: a) TEM dark field micrograph of MITR irradiated Cr coating taken with 200 keV electrons. Cr, O, and C elemental maps (b, c, and d, respectively) of a) showing uniform distribution of impurities and no evidence for second phase formation.

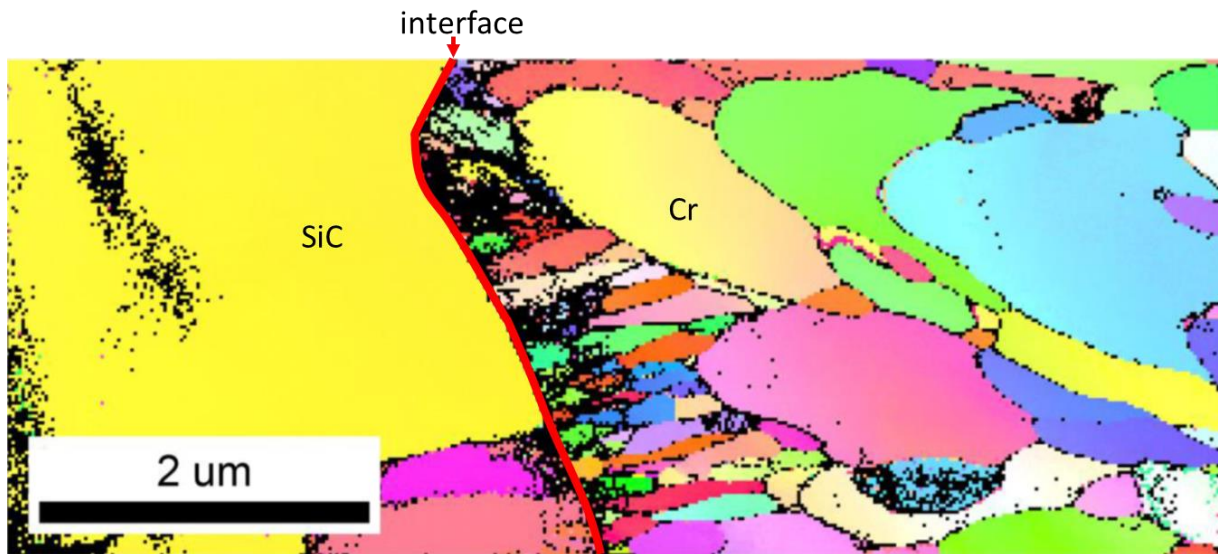


Figure 4.54: Inverse pole figure of MITR irradiated Cr coating on CVD SiC, as obtained by TKD. A red line has been superimposed on the figure to indicate the position of the interface.

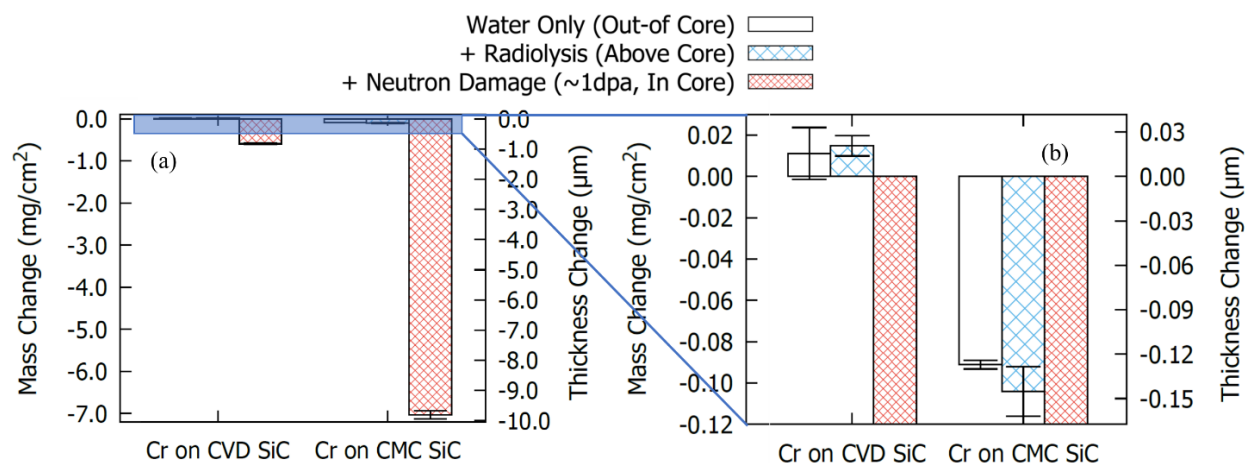


Figure 4.55: Mass change of SiC samples with Cr coating exposed to recirculating PWR water in three positions within the MITR: in-core, above-core, and out-of-core. a) full scale, and b) detailed scale.

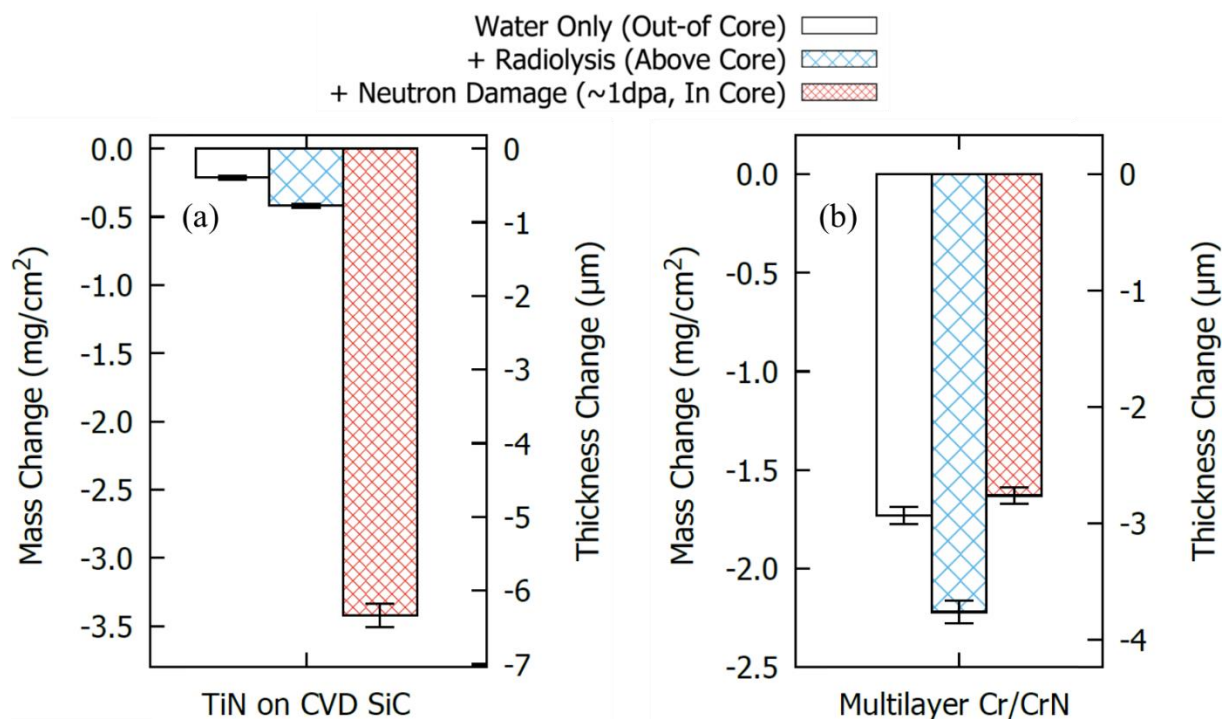


Figure 4.56: Mass change of (a) TiN and (b) Cr/CrN multilayer coatings exposed to recirculating PWR water in three positions within the MITR: in-core, above-core, and out-of-core. Specifics of the exposure are provided in Table 3.

attack, spallation, and formation of oxides is not considered in that evaluation. Mass change of uncoated SiC exposed in these conditions is reported in another study [104]. For purposes of comparison, the mass change of monolithic SiC was approximately -0.01 mg/cm^2 , -0.03 mg/cm^2 , and -0.06 mg/cm^2 in the out-of core, above core, and in core regions, respectively.

Figure 4.55 shows the changes to Cr coatings on CVD and CMC SiC in (a) full scale, and (b) zoomed in to show the finer detail. The CVD-coated SiC had a net mass gain, except where exposed to neutron radiation damage, where the sample lost approximately 0.6 mg/cm^2 . The Cr on CMC lost mass in every condition, with a nearly 70x increase in the mass loss in the presence of radiation damage.

Figure 4.56 shows the mass change of the (a) TiN coating and (b) Cr/CrN multilayer coating. The TiN sample lost mass in every case, corresponding to about $0.5 \text{ }\mu\text{m}$ and $1 \text{ }\mu\text{m}$ for the out-of-core and above core samples, respectively. The in-core sample lost an amount of mass consistent with a complete loss of the coating. The Cr/CrN samples lost significant mass in each case, with no correlation to the exposure condition.

Figure 4.57 and Figure 4.58 show optical surface and SEM cross-sectional microscopy, respectively, of the TiN-coated CVD SiC samples after exposure. As shown in Figure 4.57, the post-exposure surface of the in-core sample differed markedly from the above- and out-of-core samples. XRD (not shown) examination did not reveal any TiN peaks on the in-core sample, indicating that the entire TiN coating was lost (consistent with the mass change data in Figure 4.56). Thus, no cross-section of the in-core TiN-coated sample was obtained. The cross-sections of the above and out-of-core samples revealed a well-adhered TiN coating with a thin layer of TiO_2 on the surface, as confirmed by SEM-EDS. No cracking on these samples was observed. Figure 4.58 presents data from samples exposed above and out-of core.

Extensive cracking and coating spallation was observed on the CrN/Cr-coated samples in by surface optical microscopy (Figure 4.59) and cross-sectional SEM (Figure 4.60) for all three exposure conditions. While some areas were visible in cross-section where the coating was not spalled, these areas showed significant coating cracking. Representative cross-section images (Figure 4.60) showed no coating on most of the samples. This observation of pronounced spallation of the CrN/Cr coating is consistent with the large mass losses observed for all three exposure conditions in Figure 4.56.

Figure 4.61 and Figure 4.62 reveal the Cr coating to be adherent and uncracked on the above-core and out-of-core samples. Select areas of coating cracking were observed, however, these were localized and appeared to be related to underlying SiC defects. The images shown are representative of most of the observed regions. The in-core samples appeared to be significantly cracked with few well-adhered regions. Over 90% of the interface appeared cracked (Figure 4.62a) with many cracks normal to the interface as well, even in regions where the coating was not separated from the surface. The cracks observed in the sample substrates were typical across all coating types in both as-received and exposed samples.

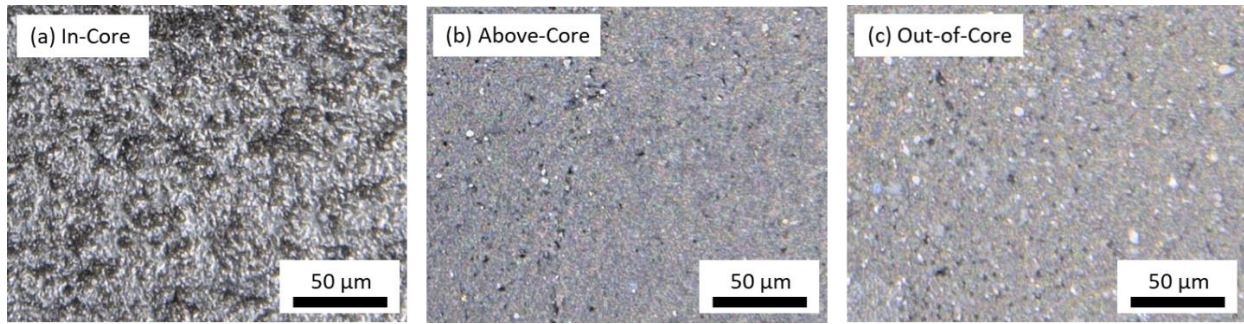


Figure 4.57: Optical micrographs of the surface of CVD SiC samples with TiN coating exposed in the MITR a) in-core, b) above-core, c) out-of-core, as defined in Table 3.

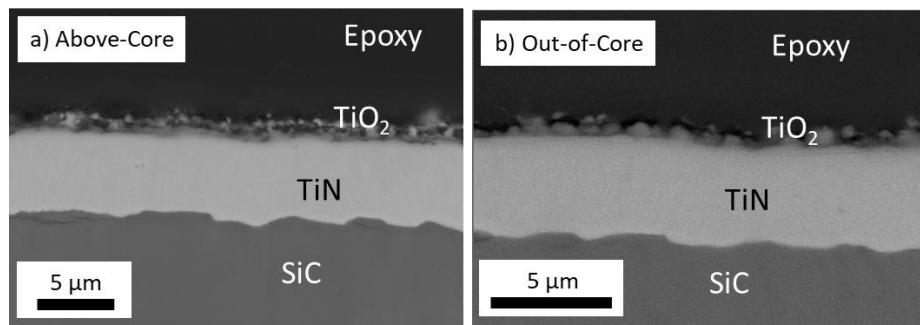


Figure 4.58: Cross-sectional SEM-BSE micrographs of TiN coating on CVD SiC exposed in the MITR a) above-core, and b) out-of-core, as defined in Table 3. In-core cross-sections were not performed for reasons discussed in the text.

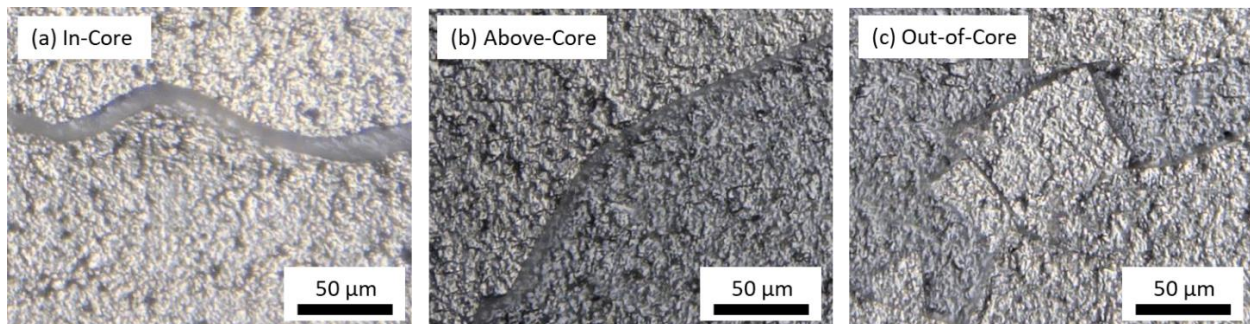


Figure 4.59: Optical micrographs of the surface of CVD SiC samples with Cr/CrN coating exposed in the MITR a) in-core, b) above-core, c) out-of-core, as defined in Table 3.

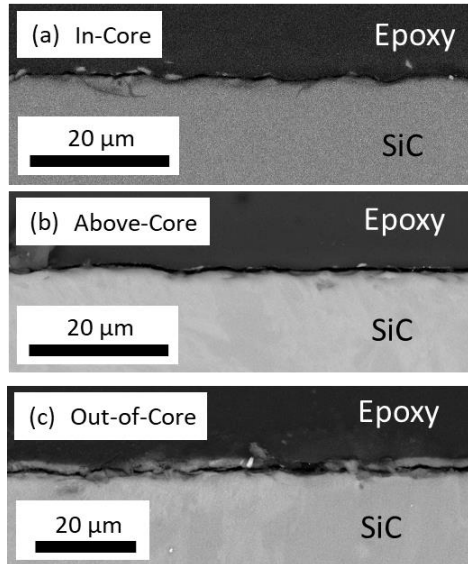


Figure 4.60: Cross-sectional SEM-BSE micrographs of CVD SiC with Cr/CrN coating exposed in the MITR a) above-core, and b) out-of-core, as defined in Table 3

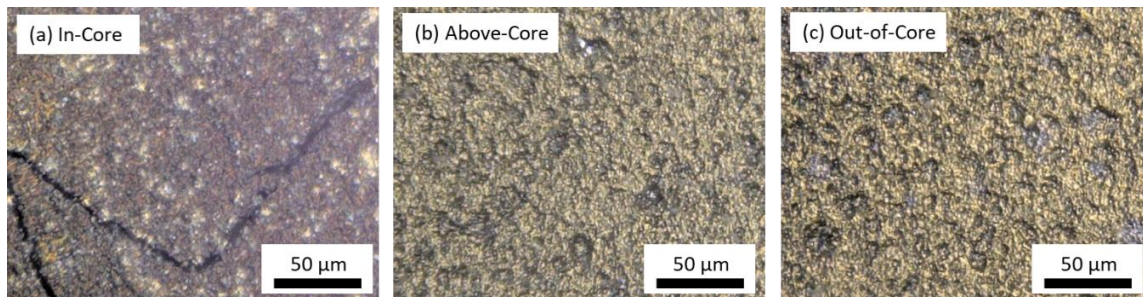


Figure 4.61: Optical micrographs of the surface of CVD SiC samples with Cr coating exposed in the MITR a) in-core, b) above-core, c) out-of-core, as defined in Table 3.

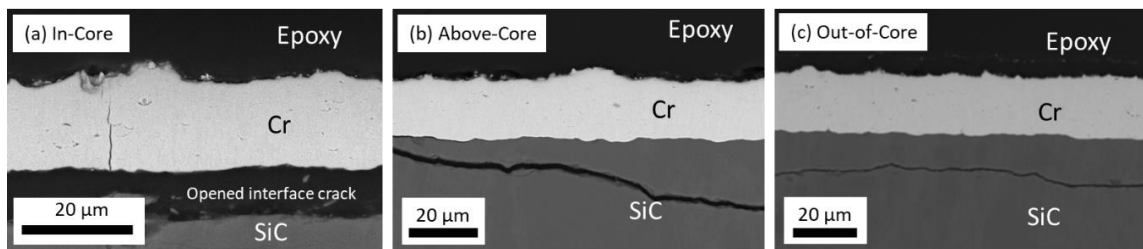


Figure 4.62: Cross-sectional SEM-BSE micrographs of CVD SiC with Cr coating exposed in the MITR a) above-core, and b) out-of-core, as defined in Table 3

Chapter 5: A Note on Chemical Kinetics: Extracting Meaningful Standard Enthalpies and Entropies of Activation for Surface Reactions from Kinetic Rates

5.1 Introduction and Value to this Work

In the discussion of the results following this chapter, some discussion will be given to the use of Transition State Theory (TST) in the evaluation of the chemical kinetics of SiC. Given the relative obscurity of this theory in engineering practice and inconsistencies in its implementation, in corrosion science particularly, a method is developed in this chapter to more accurately implement this chemical kinetics theory in a meaningful way, allowing for better confidence in the mechanistic insights. This chapter will be published in the form it is found here as ref. [151].

In the 1800s, substantial effort was dedicated to developing a general model for chemical kinetics [152, 153]. By the early 1900s, a variety of theories existed with varied applicability, most only relevant to specific chemical systems [154, 155]. Of these, the well-known Arrhenius formulation, Eqn. 5.1, was the most applicable across all or nearly all systems [152]

$$Rate = k \prod_i^m C_i^{n_i} = A e^{-\frac{E_a}{RT}} \prod_i^m C_i^{n_i} \quad \text{Eqn. 5.1}$$

In Eqn. 5.1, the *Rate* is the measured reaction rate in convenient units (e.g., mol L⁻¹ s⁻¹, see reference [156] for further discussion), *k* is the rate constant *A* is a pre-exponential factor originally assumed to be independent of concentration and temperature, *E_a* is the activation energy, *R* is the universal gas constant, *T* is the absolute reaction temperature. The $\prod$ term is the product of each of the concentrations, *C_i*, for each of the *m* reacting species, raised to that species respective reaction order, *n_i* (see reference [156] for further discussion). As presented here, the units of the rate are set to the depletion/production of a single species per unit time, $\frac{u_d}{u_t}$ where *u_d* is proportional to a density of a single species and *u_t* are units of time such as seconds. The units of the rate constant, *u_k*, are defined as being whatever units are necessary to produce a *Rate* with the desired units. That is, by definition, $u_k = \frac{u_r}{u_{[reactants]}} = \frac{u_d}{u_t u_{[reactants]}}$, where *u_[reactants]*

represents the aggregate units of the $\prod$ term. The term $A e^{-\frac{E_a}{RT}}$ is defined as being equal to the rate constant, *k*, and has units of *u_k*. For example, take the generic reaction $B \xrightleftharpoons[k_b]{k_f} D + E$

operating with elementary reaction orders. If looking at the rate of depletion of species B with units of M for concentration and seconds for time, the units of *Rate_{deplete}* = -d[B]/dt will be *u_r*=M s⁻¹. The net reaction has a rate equation of *Rate* = *k_f*[B] – *k_b*[D][E]. If all other concentrations have the same units, it follows that *u_{k_f}*=s⁻¹ and *u_{k_b}* = M⁻¹ s⁻¹. At equilibrium, the rate of depletion of any species is zero with *k_f*[B] = *k_b*[D][E]. This yields a kinetic equilibrium constant, $K = \frac{k_f}{k_b} = \frac{[D][E]}{[B]}$ (the concept of a thermodynamic equilibrium constant is noted later in this manuscript).

The above formulation finds broad application in scientific and engineering studies. The Arrhenius equation provides the predictive power required by engineering, while also yielding physico-chemical knowledge via the energy barrier (E_a), which is useful for directly and quantitatively comparing different systems. Typically, the Arrhenius equation is applied by rearranging equation Eqn. 5.1 to equation Eqn. 5.2 and plotting the data as the left-hand side versus $1/T$. The activation energy then falls out from the slope, and the pre-exponential factor falls out from the intercept².

$$\ln\left(\frac{Rate}{u_k \prod_i^m C_i^n}\right) = \ln\left(\frac{A}{u_k}\right) - \frac{E_a}{RT} \quad \text{Eqn. 5.2a}$$

$$\ln\left(\frac{k}{u_k}\right) = \ln\left(\frac{A}{u_k}\right) - \frac{E_a}{RT} \quad \text{Eqn. 5.2b}$$

The units of the pre-exponential factor are the same as the units of the rate constant. Arrhenius plots are often described as plotting $\ln(k_i)$ vs. $1/T$ or $\ln(Rate_i)$ vs. $1/T$, but such a description is necessarily incorrect when careful attention is paid to units, as one cannot take the log of a quantity that has units. It is mathematically necessary to cancel the units of k or $Rate$ in the logarithm, such that a rate constant Arrhenius plot is more correctly described as $\ln\left(\frac{k}{u_k}\right)$ vs $1/T$, where u_{k_i} are the units of the rate constant. Careful inclusion of the u_k term makes clear that the extracted intercept can then be converted between units. It is therefore recommended that publications explicitly note the u_k term when creating Arrhenius plots in order to avoid unit errors in interpreting the intercept [163]. A weakness of the Arrhenius framework, however, is that the pre-exponential factor, A , is not required to carry any physical meaning. Of the various attempts to assign meaning to this factor, collision theory and conventional transition-state theory (TST) have met with the most success. In the next section, the authors describe the fundamentals of transition state theory, and how to standardize and apply TST with respect to

²Strictly speaking, the Arrhenius equation is an empirical equation, and only provides direct physico-chemical knowledge when the kinetics are reflective of a single chemical elementary step. When those two conditions are not met, physico-chemical knowledge cannot be directly inferred with confidence from parameters extracted by fitting to the Arrhenius form. The energetic span model can help assess whether the kinetics observed are reflective of an elementary step, and in general microkinetic modeling may be required to assess the degree of rate control of individual elementary steps. For systems where the molecules are well-mixed and where a single chemical elementary step has a high degree of rate control, an empirical fitting to the Arrhenius form provides physico-chemical information. See, [157] S. Kozuch, S. Shaik, How to Conceptualize Catalytic Cycles? The Energetic Span Model, *Accounts of Chemical Research* 44(2) (2011) 101-110, [158] S. Kozuch, A refinement of everyday thinking: the energetic span model for kinetic assessment of catalytic cycles, *Wiley Interdisciplinary Reviews: Computational Molecular Science* 2(5) (2012) 795-815, [159] A. Savara, I. Rossetti, C.E. Chan-Thaw, L. Prati, A. Villa, Microkinetic Modeling of Benzyl Alcohol Oxidation on Carbon-Supported Palladium Nanoparticles, *ChemCatChem* 8(15) (2016) 2482-2491, [160] S. Matera, W.F. Schneider, A. Heyden, A. Savara, Progress in Accurate Chemical Kinetic Modeling, Simulations, and Parameter Estimation for Heterogeneous Catalysis, *ACS Catalysis* 9(8) (2019) 6624-6647, [161] C. Stegelmann, A. Andreasen, C.T. Campbell, Degree of Rate Control: How Much the Energies of Intermediates and Transition States Control Rates, *Journal of the American Chemical Society* 131(23) (2009) 8077-8082, [162] C.T. Campbell, The Degree of Rate Control: A Powerful Tool for Catalysis Research, *ACS Catalysis* 7(4) (2017) 2770-2779..

surface reactions even without understanding of the fundamentals. Finally, the authors provide real examples and a summary.

5.2 Application of Transition State Theory

5.2.1 Background and Fundamental Equation of Transition State Theory

TST applies to individual elementary reaction steps separately (it cannot be applied directly to a “total reaction”) and begins with the assumption that a quasi-equilibrium is formed between the reactants and the rate-limiting activated complex [152, 153, 156, 164, 165]. Effectively, this requires applying it to a single chemical reaction elementary step (such as breaking or forming of a crucial chemical bond), and that this step not proceed so rapidly as to invalidate the Boltzmann energy distribution of the reactant molecules involved in that elementary step [166, 167].

Transition state theory provides physical meaning for the pre-exponential factor, A . For simplicity, the authors present the case where the rate corresponds to depletion of a species with a reaction order of 1. In the conventional thermodynamic formulation of TST [152], the key factor is that each molecule of the transition state crosses a barrier at a velocity given by $\frac{k_B T}{h}$. Then, considering the transition state to be an intermediate ‘product’ of the reactants, a thermodynamic equilibrium constant (further explained below) enables substituting for the concentration of the transition state using a conventional equilibrium equation [168], yielding the form in Equation 3.

$$\begin{aligned} k &= \kappa \frac{k_B T}{h} [TS] = \kappa \frac{k_B T}{h} e^{-\frac{\Delta^\ddagger G^\circ}{RT}} \frac{\gamma_{TS}}{\gamma_R} \frac{(c_{TS}^\circ)^{-1}}{(\prod_i^m (c_{R_i}^\circ)^{n_i})^{-1}} \\ &= \kappa \frac{k_B T}{h} e^{-\frac{\Delta^\ddagger H^\circ}{RT} + \frac{\Delta^\ddagger S^\circ}{R}} \frac{\gamma_{TS}}{\gamma_R} \frac{(c_{TS}^\circ)^{-1}}{(\prod_i^m (c_{R_i}^\circ)^{n_i})^{-1}} \end{aligned} \quad \text{Eqn. 5.3}$$

where, k is the rate constant, $[TS]$ is the concentration of the transition state, k_B is the Boltzmann constant, T is the reaction temperature, h is the Planck constant, R is the universal gas constant, and κ is the transmission coefficient [153, 166, 169]. κ is a unitless fraction that includes the effects of tunneling (which increases the reaction rate) and reflection back after crossing the barrier (which decreases the reaction rate) [166]. For experimentalists, the value of κ is generally taken to be 1 unless there is existing knowledge otherwise. It can be shown using Eqn. 5.14 from later in the manuscript that an error of under-estimating κ by a factor of 3 will translate to an error in $\Delta^\ddagger S^\circ$ of about $-9 \frac{J}{mol \cdot K}$. Such an error is relatively small and will usually not invalidate resulting conclusions about the mechanism. The c_{TS}° and $\prod_i^m (c_{R_i}^\circ)^{n_i}$ terms represent the standard state concentrations of the transition state and reactions, respectively³. A consequence of transition state theory is that it sets the unit of the intrinsic rate constant as equal to or proportional to the concentration of the transition state, and consequently as proportional to or equal to the ratio of standard state terms in equation 3 (see numbered list at end of section 5.2

³ For example for $A + B \rightarrow C$, writing a thermodynamic equilibrium constant with transition states and rearranging for $[TS]$ we find: $\kappa \frac{k_B T}{h} [TS] = \kappa \frac{k_B T}{h} (K_{TS}^\circ)^{-1} [A][B] * \frac{[TS]^\circ}{[A]^\circ[B]^\circ} = k * [A][B]$

for more explanation). The fact that the theory sets (or restricts) the units of the rate constant is a difference relative to the Arrhenius equation, and is tied to transition state theory giving meaning to the pre-exponential term, A , as described in the next section. However, the intrinsic rate constant can be scaled by an arbitrary coefficient to change units to a phenomenological (or “observed”) rate constant, as will be explained later. For simplicity, $\prod_i^m (c_{R_i}^\circ)^{n_i}$ is represented simply as c_R° throughout the remainder of this manuscript, such that the standard states term becomes $\frac{(c_{TS}^\circ)^{-1}}{(c_R^\circ)^{-1}}$. The terms γ_{TS} and γ_R are the activity coefficient terms for the transition state and the reactant state, respectively (where γ_R comprises a product of terms for each reactant, much like c_R°). The terms γ_{TS} and γ_R are typically taken to be unity. $\Delta^\ddagger S^\circ$, $\Delta^\ddagger G^\circ$, $\Delta^\ddagger H^\circ$ are the standard entropy of activation, standard Gibbs free energy of activation, and standard enthalpy of activation, respectively [153, 166]. As defined here, the thermodynamic values ($\Delta^\ddagger S^\circ$, $\Delta^\ddagger G^\circ$, $\Delta^\ddagger H^\circ$) exclude the degrees of freedom in a transition state that would be associated with an activated complex moving over a saddle point [156] such as the vibration associated with a bond breaking. These are the *molecular* thermodynamic terms and are usually expressed as molar quantities. They should not be confused with the total enthalpy, entropy, and Gibbs free energy of the system (which includes non-chemical changes). Additionally, while some sources use wording such as “activation entropy”, “activation enthalpy” etc., the authors recommend following the IUPAC recommendations for naming: standard entropy of activation and standard enthalpy of activation. While these names are longer, they emphasize that the standard state plays a role in these values. In cases where the standard enthalpy of activation and standard entropy of activation can be approximated as being constant across a finite temperature range being studied, the values can be extracted by making an Arrhenius plot, which includes the standard state for the transition state and the product of the set of standard state values for each reactant [170-172]. It is readily apparent that for an arbitrary total reaction order, n_t , the units of the denominator of the standard state term will have units such as concentration to the power of n_t , similar to the units of the concentrations, $u_{[reactants]}$, in the rate equation. The expected rate constant units are fully obtained when it is noted that units of inverse time emerge from the $k_B T/h$ term related to the velocity for crossing the activation barrier, yielding the same units as before: $u_k = \frac{u_r}{u_{[reactants]}} = \frac{u_d}{u_t u_{[reactants]}}$.

In practice, the forgoing means that after the intercept of an Arrhenius plot is obtained, it is possible to extract $\Delta^\ddagger S^\circ$, and also that expressing the rate constant with units matching those of the standard state can be convenient. The value of $\Delta^\ddagger S^\circ$ does depend on the choice of the standard state [171]. Unfortunately, many textbooks and publications omit explicit writing of the standard state, c° , terms, resulting in confusion [156, 173]⁴.

⁴ The authors note that TST can also be applied using a statistical mechanical formulation based on solely a Boltzmann distribution and absolute energy difference. That formulation does not require the use of standard states and will not be presented here (the absolute energy formulation can be applied for special cases when one additionally knows the number of particles rather than solely concentrations and is thus not practical for most experimental systems). See refs [153] K.J. Laidler, J.H. Meiser, B.C. Sanctuary, Physical Chemistry, 4th ed., Brooks Cole 2002, [166] D.G. Truhlar, Transition state theory for enzyme kinetics, Archives of Biochemistry and

In general, as illustrated in section 5.1, a kinetic equilibrium constant can be given by k_t/k_r , but the thermodynamic derivation of TST is based on a standard equilibrium constant, K° , which is a thermodynamic equilibrium constant and is given by $k_f(c_f^\circ)^{-1}/k_r(c_r^\circ)^{-1}$ where the (c_f°) and (c_r°) terms are the standard states associated with the reactants and products, respectively [174]. The concept of the thermodynamic equilibrium constant should not be confused with a kinetic equilibrium constant. A kinetic equilibrium constant may have units, but a thermodynamic equilibrium constant must be unitless and can be related to a free energy of reaction, such that the standard free energy of reaction is related via $\Delta G^\circ = -RT \ln (K^\circ)$: the importance of this definition is that the standard states provide reference states for the activities of species, and the ratios of species at equilibrium are related to the Gibbs free energy of reaction via the chemical potential (as further explained in reference [168, 175]).

Thermodynamics often requires analysis relative to a reference state, generally taken to be based on the chemical potential of a given species at a standard state. As noted by Savara [170]:

“The reference state can sometimes be arbitrarily chosen but must have a specified pressure and temperature, as well as specification of other attributes that are necessary to define the state thermodynamically unambiguously (for example, the number of molecules or volume could be required for certain situations). Standard states are specific sets of reference states that are adopted as a convention for use by society or subsets of the scientific community. Standard states enable tabulation and facile comparison of thermodynamic data obtained from differing experiments or theory for varied substances and reactions. Note that universal use of the same standard state(s) is not mathematically or physically necessary but is societally desirable.”

The standard state is generally a hypothetical state with perfect or ideal behavior (this point is discussed further in the appendices in the associated published article [151], where the interested reader is referred). In this manuscript, a method to apply transition state theory to surface reactions is described for the intended audience of applied researchers.

5.3 Using Transition State Theory with Empirical Data

Once the standard states are chosen for the reactant states and transition state, it is possible to obtain the thermodynamic parameters associated with the transition state. In practice, it is convenient to get E_a and to then get the thermodynamic quantities after. It can be shown [153] that,

$$E_a = \Delta^\ddagger H^\circ - P\Delta^\ddagger V^\circ + RT \quad \text{Eqn. 5.4}$$

where $\Delta^\ddagger V^\circ$ is the standard volume change in going from the initial to the activated state. It should be emphasized that unlike the Arrhenius equation, the TST equations only apply to elementary steps, and that the $\Delta^\ddagger V^\circ$ is between the reactant and transition state (not ΔV° when going from reactant to products). Thus, for an elementary step which may involve either a gas phase reactant or a transition state, it is necessary to know (or to assume) whether the transition state is more like the reactant or not, to assess the value of $\Delta^\ddagger V^\circ$. Rearranging and substituting into Eqn. 5.3 yields the general usable form of the Eyring equation,

Biophysics 582 (2015) 10-17, [170] A. Savara, Standard States for Adsorption on Solid Surfaces: 2D Gases, Surface Liquids, and Langmuir Adsorbates, The Journal of Physical Chemistry C 117(30) (2013) 15710-15715.

$$k = \kappa \frac{k_B T}{h} e^{-\frac{E_a}{RT} - \frac{P\Delta^\ddagger V^\circ}{RT} + \frac{\Delta^\ddagger S^\circ}{R} + 1} \frac{\gamma_{TS} (c_{TS}^\circ)^{-1}}{\gamma_R (c_R^\circ)^{-1}} \quad \text{Eqn. 5.5}$$

The functional forms of equations Eqn. 5.2 and Eqn. 5.5 allow relation of the pre-exponential factor of the Arrhenius equation to TST, revealing that A has a temperature dependence in TST. By approximating $\Delta^\ddagger S^\circ$ and $\Delta^\ddagger H^\circ$ as independent of temperature⁵ then a pre-exponential factor, A , can be extracted.

$$A = \kappa \frac{k_B T}{h} e^{1 - \frac{P\Delta^\ddagger V^\circ}{RT} + \frac{\Delta^\ddagger S^\circ}{R}} \frac{\gamma_{TS} (c_{TS}^\circ)^{-1}}{\gamma_R (c_R^\circ)^{-1}} \quad \text{Eqn. 5.6}$$

The middle term of the exponential, $\frac{P\Delta^\ddagger V^\circ}{RT}$, is evaluated as follows. For reactions between solids, in solutions, and for unimolecular gas reactions $P\Delta^\ddagger V^\circ \approx 0$. For reactions with a change in the number of gas molecules, the ideal gas law ($P\Delta^\ddagger V^\circ = \Delta^\ddagger n^\circ RT$) suggests that the middle term approximately equals the stoichiometric change in gas phase molecules when going from the reactant to the transition state multiplied by RT . This term matters when going from a gas phase reactant to a condensed phase transition state, for example.

Within the Arrhenius framework, determination of E_a and A is sometimes accomplished empirically by plotting $\ln\left(\frac{\text{Rate}}{u_r}\right)$ versus the inverse of absolute temperature. However, within TST, from Eqn. 5.6, A is expected to have a linear dependence on T for cases where $\Delta^\ddagger V^\circ \approx 0$, and where $\Delta^\ddagger S^\circ$ and $\Delta^\ddagger H^\circ$ are approximately independent of temperature. Substitution of Eqn. 5.5 into Eqn. 5.1 and re-arranging yields the final equation, Eqn. 5.7, which can be re-arranged into Eqn. 5.8.

$$\text{Rate} = \frac{k_B T}{h} e^{\frac{\Delta^\ddagger S^\circ}{R} + 1 - \frac{P\Delta^\ddagger V^\circ}{RT}} e^{-\frac{E_a}{RT}} \prod_i^m C_i^n \frac{\gamma_{TS} (c_{TS}^\circ)^{-1}}{\gamma_R (c_R^\circ)^{-1}} \quad \text{Eqn. 5.7}$$

$$\ln\left(\frac{\text{Rate}}{T \prod_i^m C_i^n} \frac{u_T}{u_k}\right) = \ln\left(\frac{k_B u_T}{h u_k} e^{\frac{\Delta^\ddagger S^\circ}{R} + 1 - \frac{P\Delta^\ddagger V^\circ}{RT}} \frac{\gamma_{TS} (c_{TS}^\circ)^{-1}}{\gamma_R (c_R^\circ)^{-1}}\right) - \frac{E_a}{RT} \quad \text{Eqn. 5.8}$$

Where u_T is unit of temperature. Plotting the data as the left side versus $1/T$ (similar to an Arrhenius plot) yields an activation energy as a function of the y-intercept, b ,

$$\Delta^\ddagger S^\circ = R \left[b + \ln\left(\frac{h u_k}{\frac{\gamma_{TS} (c_{TST}^\circ)^{-1}}{\gamma_R (c_R^\circ)^{-1}} k_B u_T}\right) - 1 + \frac{P\Delta^\ddagger V^\circ}{RT} \right] \quad \text{Eqn. 5.9}$$

The value added by and challenges of considering TST are discussed in the following sections. One of the values added is in greater expected accuracy due to the difference of $\ln\left(\frac{1}{T}\right)$ between the left sides of equations Eqn. 5.2a and Eqn. 5.8, which will affect the empirical estimation of

⁵ This is a common approximation during applications of TST. When application of TST is over small temperature ranges, this assumption is likely to hold true, but will become less valid as the temperature range is increased.

the activation energy. This difference is typically quite small and is discussed in Appendix C of the article associated with this chapter [151]. The primary strength in using TST is not in the improved temperature dependence considerations of E_a , but in its ability to extract more thermodynamic meaning from rate constants (particularly when they are measured at multiple temperatures). How to do so, and the importance of the units of the rate constant, is further described below.

5.4 Standardizing Rate Constant Units and Activities for Simpler Evaluation of Thermodynamic Properties from TST

Obtaining the most benefit from empirical TST requires considering the units of the terms presented in the previous section. Critical aspects are knowing what is the elementary step which the rate constant is reflective of, and also which units of activity the reactants and transition state are based on. Standardizing the units of the rate constant and its pre-exponential will facilitate universal application of TST and evaluation of the thermodynamic properties derived thereof. From Eqn. 5.5, which includes the standard state terms, A must include the units of inverse time, but it also includes the standard state terms, $\frac{(c_{TS}^\circ)^{-1}}{(c_R^\circ)^{-1}}$ previously described. The authors support the CODATA recommendation [176] that the time units of A always be reported with units of $[s^{-1}]$. For convenience, we define $C^\circ = \frac{(c_{TS}^\circ)^{-1}}{(c_R^\circ)^{-1}}$. Often, C° is not chosen explicitly, which implies a value of unity in reciprocal units relative to that of the rate constant. For example, if the rate constant has units of $\text{mg cm}^{-2} \text{s}^{-1}$, this would imply $[C^\circ] = \text{cm}^2 \text{mg}^{-1}$. Any choice can in principle be converted to other units for the same chemical potential, as will be demonstrated below. However, the numerical value of $\Delta^\ddagger S^\circ$ does depend on the choice of the standard state [171] so values from different studies cannot be compared directly unless the same standard states are used.

As it applies to surface reactions such as catalysis and corrosion, the surface-adsorbed states and those of the empty sites must be assigned. This is not a situation that is typically taught during classroom lessons about TST, though there has been some literature discussion [170]. For a surface where the chemical composition is invariant (such as dissolution of a pure phase with no change in composition at the surface) the surface activity is assumed to be 1, and an activity of 1 is an appropriate standard state. However, when there are multiple elementary steps which include local site changes (such as oxidation of a metal surface to a metal oxide, where sites are immobile before and after the change) then the appropriate elementary step must be identified and a lattice-based model of sites can be employed. The units and chemical potential required for the latticed base model merit a small amount of discussion. As is well known, adsorption equilibria with a lattice of sites gives adsorption and desorption rates of $k_{\text{ads}}\theta_{\text{e-sites}}P_A$ and $k_{\text{des}}\theta_{\text{ads}}$ where θ_{ads} and $\theta_{\text{e-sites}}$ represent the coverage of adsorbates and empty sites, respectively, in rtL units (fractional occupation of sites relative to number of lattice sites). For a single adsorbate situation, $\theta_{\text{ads}} = 1 - \theta_{\text{e-sites}}$. This leads to a kinetic equilibrium constant expression of:

$$K_L = \frac{k_{\text{ads}}}{k_{\text{des}}} = \frac{\theta_{\text{ads}}}{(1 - \theta_{\text{ads}})P_A} \quad \text{Eqn. 5.10}$$

This expression is often used for the specific case where activity coefficients and standard state concentrations are all unity. For a lattice-adsorbed species, the actual chemical potential is not linear with the number of molecules due to the configurational entropy associated with the lattice sites available, necessitating the use of activity coefficients (see equations in the Supporting Information of [170] and also [175]). As noted in the Supporting Information of [170], There are 2 ways of representing the activity and activity coefficient. The first way is to treat the activities of the adsorbate in the empty sites as coupled and given by relative coverages (K_{L1}° below). The second way is to treat the adsorbates and empty sites as having separate base activities fixed at 1, and to include the effects of configurations in the activity coefficient (K_{L2}° below). Note that in both cases, the standard state terms are the same, and the thermodynamics for any particular ratio of products to reactants are thus unchanged for K_{L1}° vs K_{L2}° . In essence, the two formalisms only use different units for the activity, which is separate from the choice of standard state. In both formalisms, after multiplying by the activity coefficients and standard states, the same value is obtained. A simple example will be given below.

$$K_{L1}^\circ = \frac{k_{ads} (c_f^\circ)^{-1}}{k_{des} (c_r^\circ)^{-1}} = \frac{\theta_{ads}}{\theta_{e-sites} P_A} \frac{\gamma_{ads}}{\gamma_{e-sites} \gamma_A} \frac{(c_{ads}^\circ)^{-1}}{(c_{e-sites}^\circ)^{-1} (P^\circ)^{-1}} \quad \text{Eqn. 5.11}$$

$$K_{L2}^\circ = \frac{k_{ads} (c_f^\circ)^{-1}}{k_{des} (c_r^\circ)^{-1}} = \frac{1}{1 * P_A} \frac{\gamma_{ads}}{\gamma_{e-sites} \gamma_A} \frac{(c_{ads}^\circ)^{-1}}{(c_{e-sites}^\circ)^{-1} (P^\circ)^{-1}} \quad \text{Eqn. 5.12}$$

For the first Langmuir adsorbate activity framework with K_{L1}° , the standard state can be defined as $c_{ads}^\circ = \theta_{ads}^\circ = 0.5$ rtL and $c_{e-sites}^\circ = \theta_{e-sites}^\circ = 0.5$ rtL, such that $\theta_{ads}^\circ = \theta_{e-sites}^\circ$ and the terms cancel (though the choice of 0.5 rtL and setting $c_{ads}^\circ = c_{e-sites}^\circ$ is not necessary in the first framework). For the second activity framework with K_{L2}° the concentrations of the adsorbates and the empty sites are each taken to be 1 and unitless (as is commonly done for a solid in equilibrium with a solution), such that $c_{ads}^\circ = c_{e-sites}^\circ = 1$ and any coverage dependence (even the linear coverage dependence of an ideal adsorbate) is contained within the activity coefficients. The usage of the two frameworks is most easily demonstrated with a pair of simple examples.

Consider a gas reaction on a solid where the standard state corresponds to a coverage of 0.5 rtL for each framework (note that in both frameworks, the standard state must still be defined as a real coverage as the activity depends on real coverage). Using the simplifying assumption that the activity of both the empty sites and adsorbates will be linear with coverage, consider an experiment where $\theta_{ads} = 0.75$ rtL and $\theta_{e-sites} = 0.25$ rtL. Within the first framework, evaluation of the non-pressure terms proceeds as follows:

$$K_{L1}^\circ = \frac{\theta_{ads}}{\theta_{e-sites}} \frac{\gamma_{ads}}{\gamma_{e-sites}} \frac{(c_{ads}^\circ)^{-1}}{(c_{e-sites}^\circ)^{-1}} = \frac{0.75 \text{ rtL}}{0.25 \text{ rtL}} * \frac{1}{1} * \frac{(0.5 \text{ rtL})^{-1}}{(0.5 \text{ rtL})^{-1}}$$

Within the second framework, evaluation of the non-pressure terms proceeds as follows. With the standard state terms of both empty and adsorbed sites being 1, the activity coefficients become $\gamma_{ads} = \frac{\theta_{ads}}{c_{ads}^\circ} = \frac{0.75}{0.5} = 1.5$ and $\gamma_{e-sites} = \frac{\theta_{e-sites}}{c_{e-sites}^\circ} = \frac{0.25}{0.5} = 0.5$. This is because the

activity of $\theta_{\text{ads}} = 0.75$ rtL is 1.5 times that of $\theta_{\text{ads}} = 0.50$ rtL and the activity of $\theta_{\text{e-sites}} = 0.25$ rtL is 0.5 times that of $\theta_{\text{e-sites}} = 0.50$ rtL. Therefore,

$$K_{L_2}^{\circ} = \frac{1}{1} \frac{\gamma_{\text{ads}}}{\gamma_{\text{e-sites}} \gamma_A} \frac{(c_{\text{ads}}^{\circ})^{-1}}{(c_{\text{e-sites}}^{\circ})^{-1}} = \frac{1}{1} * \frac{1.5}{0.5} * \frac{(1)^{-1}}{(1)^{-1}}$$

In both frameworks, the final ratio is the same (and is 3 for the above example).

Now consider a more complex example. Again, let the standard state correspond to a coverage of 0.5 rtL for each framework (note that in both frameworks, the standard state must still be defined as a real coverage as the activity depends on real coverage) with the same coverages: $\theta_{\text{ads}} = 0.75$ rtL and $\theta_{\text{e-sites}} = 0.25$ rt. However, in this case the activity of adsorbates is non-linear with coverage, such that the adsorbate is three times as active at $\theta_{\text{ads}} = 0.75$ rtL as at $\theta_{\text{ads}} = 0.50$ rtL (a two-fold increase in activity from the linear case). The empty sites are still half as active at $\theta_{\text{e-sites}} = 0.25$ rtL compared to $\theta_{\text{e-sites}} = 0.50$ rtL, as before. Within the first framework, evaluation of the non-pressure terms proceeds as follows:

$$\frac{\theta_{\text{ads}}}{\theta_{\text{e-sites}}} \frac{\gamma_{\text{ads}}}{\gamma_{\text{e-sites}}} \frac{(c_{\text{ads}}^{\circ})^{-1}}{(c_{\text{e-sites}}^{\circ})^{-1}} = \frac{0.75 \text{ rtL}}{0.25 \text{ rtL}} * \frac{2}{1} * \frac{(0.5 \text{ rtL})^{-1}}{(0.5 \text{ rtL})^{-1}}$$

The activity coefficient is coverage dependent, and in this example the first framework receives an activity coefficient of 2 for the adsorbate at this coverage since that is the deviation from linearity.

Within the second framework, evaluation of the non-pressure terms proceeds as follows:

$$\frac{1}{1} \frac{\gamma_{\text{ads}}}{\gamma_{\text{e-sites}} \gamma_A} \frac{(c_{\text{ads}}^{\circ})^{-1}}{(c_{\text{e-sites}}^{\circ})^{-1}} = \frac{1}{1} * \frac{3}{0.5} * \frac{(1)^{-1}}{(1)^{-1}}$$

As can be seen, in the second framework, the ratio of the *absolute* activity relative to that of at the standard state is taken as the activity coefficient, directly. Both frameworks do give the same ratios and ultimately give the same results when used correctly.

The primary advantage of the first framework, with $K_{L_1}^{\circ}$, is that when setting $\theta_{\text{ads}}^{\circ} = \theta_{\text{e-sites}}^{\circ} = 0.5$ rtL, any tabulated standard entropies of adsorbates (and translationally immobile transitions states) will reflect only the internal molecular modes as the configurational terms will cancel [170, 171]. This allows for chemical information to be assessed by direct comparison of the standard entropies. Thus, adsorption and reactions on materials with different site densities can be directly compared. A second advantage is that the number of sites does not even need to be known: merely the relative coverages. A third advantage is that many studies have not explicitly carried the units of the relative coverage, and thus this choice (where the standard states and configurational entropy terms cancel) will result in standard entropies matching those of studies which were not aware of the need to include standard states for adsorbates even when using relative coverages.

In the second Langmuir adsorbate activity framework, with $K_{L_2}^{\circ}$, the standard concentration is more sensibly chosen in accordance with the principle of the dilute and noninteracting limit

where the activity would be linear with adsorbate coverage. In this case, it can be convenient to set c_{ads}° to the same value of $\sigma_{\text{ads}}^\circ$ as for a 2D gas (see above). There are several advantages to the 2nd Langmuir adsorbate activity framework. First, it enables the same standard state to apply for immobile Langmuir adsorbates as for 2D gas adsorbates. Second, it is potentially more easily extensible to cases with adsorbate dissociation and adsorbate association, because only the activity coefficient is changed when configurational contributions change (that is, with the second Langmuir adsorbate activity framework, there is no reason to consider changing the adsorbate standard state for such situations). Thirdly, this method reflects the density of sites in the standard entropy of adsorption (that is, if a surface has more spaced out sites, the standard entropy of adsorption will be affected). Fourthly, this method is likely to be more easily extractable from kinetic Monte Carlo and molecular dynamics codes. This fourth advantage may have future importance. However, there is a disadvantage to this 2nd method as it requires knowing the surface density of the sites. For small enough adsorbates that near complete packing is achievable, the density of sites can be approximated as being equal to $\sigma_{\text{ads,max}}$. At this time, the first Langmuir adsorbate activity framework with K_{L1}° is dominant, though as the field moves forward, for those who investigate molecular level interactions, it is possible that the second Langmuir adsorbate activity framework with K_{L2}° will become dominant due to the possibility of easier inclusion in kinetic Monte Carlo and molecular dynamics simulations (see next paragraph). Even when the K_{L2}° framework is used, the authors recommend that $c_{\text{ads}}^\circ = c_{\text{e-sites}}^\circ$ as this will cause the standard and configurational entropy terms to still cancel.

When it comes to adsorption on surfaces by Langmuir adsorption on specific sites, it is well-established that up to third nearest neighbors influence the adsorption binding strength and the adsorption rate [160, 177-179]. While this can in principle be incorporated by considering different local environments to be different site ensembles, we suggest incorporation of the effects of co-adsorbates into the activity coefficient (this is more consistent with the way that solvent interactions are included and also facilitates direct comparison between systems with different geometric surroundings for the active site). There are also contributions from configurational entropy considerations [180]. These adsorbate-interactions and configurational entropy considerations are unlikely to be accounted for completely in the next few years, but it is likely based on the current status of the field that a few studies incorporating such terms will appear in the next 5 years. When this happens, K_{L2}° may become a more convenient framework.

Activities are also important to consider for association and adsorption reactions in solution, when bulk concentrations are used for the activities of the reactants (and consequently transition states). While it is clear that the kinetics of reactions in solution are generally proportional to the concentrations of the reactant, this may not be true for the thermodynamic activities. Historically, one description of the translational entropy of molecules in solution was to assume that they had the same three-dimensional freedom as 3D gas molecules (that is, as described by the Sackur-Tetrode equation) [181-183]. In this case, the chemical potential would scale with the number of molecules in solution and an activity coefficient remaining at approximately 1 might be possible over arbitrary concentration ranges. However, studies of association in solution suggest that the entropy change from association reactions is much smaller than would be predicted if the solutes were well described as having complete three dimensional freedom, and these studies suggest

that solute molecules have an entropy corresponding to a confined/lesser free volume [181-183]. This suggests that the partial molar entropy of solute molecules does not scale with the number of molecules (like for immobile Langmuir adsorbates, as described in the Supporting Information of [170]). Thus, the activity coefficients for solutes in association reactions and adsorption to surfaces may begin to approach 0 when very high concentrations are reached and may depend upon the absolute volume of the container. More work needs to be performed on this long-standing question, but a recommendation of using activity as proportional to concentration and with an activity coefficient value of 1 should be valid for association of solutes in very dilute solutions (e.g., < 1% by volume). This recommendation should also hold true for molecules adsorbing from a liquid to a surface.

As described, a large number of terms and assumptions are required to appropriately apply transition state theory. Unlike in use of the Arrhenius equation, the assumptions of transition state theory will result in base units for the rate constant. To facilitate improved and more widespread adoption, the authors provide the following guidance.

- 1) Always begin with reporting Eqn. 5.3 when using transition state theory within a manuscript, and then state each approximation or assumption explicitly.
- 2) Ensure that the rate constant being analyzed is reflective of a single chemical elementary step (that is, a single bond forming or breaking, or a concerted forming/breaking of bonds). If an apparent rate constant is being approximated as reflecting the rate constant of a single elementary step, then this approximation (and which elementary chemical step is being assumed to be reflected in the apparent rate constant must be reported). Generally, the elementary step should not be more than second order.⁶
- 3) Specify the phase of the elementary step reactants and transition state. For example, one might specify two gas phase molecules as reactants and a single gas phase complex as a transition state. Another example might be a single liquid phase solute molecule as the reactant and an immobile (a non-2D gas) surface bound complex as the transition state. A third example that might occur in dissolution would be an immobile surface-bound intermediate as the reactant of the elementary step and an immobile surface-bound transition state.⁷

⁶ An elementary step is almost never greater than second order. For example, $A+B \rightarrow D$ and $A^2 \rightarrow E$ are each second order. $A + B + C \rightarrow D$ and $A^2 + B \rightarrow E$ are each third order and would generally not be a permissible for elementary steps. A pre-equilibrium that results in an apparent third order reaction due to substitution of concentrations is not unusual (as described in chemical kinetics and physical chemistry textbooks), but the distinction is important as it will affect the units of the rate constant. If a practitioner believes they have a third order elementary step, they should consult a chemical kinetics specialist.

⁷ As noted under equation 3, the units of the intrinsic rate constant will be dictated by the concentration of the transition state, but can be scaled arbitrarily. This is among the reasons why standardization of units for rates is desirable. For example, with an elementary step of $A + B \rightarrow C$, the intrinsic rate constant has units of $[TS]/u_t$ but the phenomenological (“observed”) rate constant would have units sets by the rate. Consider the situation where the transition state is a surface species and has concentration units mol m^{-2} , B is a type of site and has concentration units of mol m^{-2} , and A is a solute with concentration units of mol m^{-3} . $d[A]/dt$ and $d[B]/dt$ will have different units, and thus rate equations with different units for phenomenological rate constant. From equation three, the intrinsic rate constant will have units of $\text{mol m}^{-2} \text{s}^{-1}$. If monitoring $d[B]/dt$ in $\text{mol m}^{-2} \text{s}^{-1}$, the phenomenological rate will have

- 4) In the absence of other information, use the following approximations: set $\kappa = 1$, set all $\gamma_i = 1$.
- 5) Assume $\Delta^\ddagger H^\circ$ and $\Delta^\ddagger S^\circ$ are independent of temperature.
- 6) Assume that in Eqn. 5.4 the $P\Delta^\ddagger V^\circ$ term is 0 unless there is a loss of gas molecules between the reactants and transition state (e.g., gas phase association or gas phase adsorption). Generally speaking, this means the $P\Delta^\ddagger V^\circ$ term can be safely set to 0 for reactions in liquids.
- 7) Report rate constants with the time units of s^{-1} (that is, set $u_t = 1 \text{ s}$)
- 8) Define the choices of reactant and transition state standard states that will be used.
 - a. For gas phase species, use pressure in lieu of concentration such that $c_i^\circ = P^\circ = 1 \text{ bar}$
 - b. For solutes in solution [184], use $c_i^\circ = 1 \frac{\text{mol}}{\text{L}}$ or $c_i^\circ = 1 \frac{\text{mol}}{\text{kg}}$
 - c. For immobile adsorbate species in Langmuir adsorption, use relative coverage such that $c_{iads}^\circ = \theta_{ads}^\circ = \theta_{e-sites}^\circ$. Values of 1 rtL and 0.5 rtL are each acceptable.
 - d. For cases with a 2D gas, use $c_i^\circ = \sigma_{ads}^\circ = 1.39 \times 10^{-7} \text{ mol m}^{-2}$ (it is assumed that most studies will not consider this possibility)
- 9) Use Eqn. 5.8 to obtain the activation energy and standard entropy of activation, then use equation Eqn. 5.4 to obtain the standard enthalpy of activation.

5.5 Illustration of the Need for Use of Consistent Surface States and Units

As noted in section 5.2, the choice of a standard state for the surface is critical to the quantitative interpretation of results and direct comparison between studies. This is particularly true in the field of corrosion science where great disparity in the standard state choice has inadvertently occurred. To illustrate this, Table 5.1 and Table 5.2 contain the results of a few recent studies in corrosion and catalysis, respectively. For each of these studies, the elementary step was assumed

the same units as the transition state conversion rate. However, if monitoring $d[A]/dt$, the phenomenological rate will have different units from the transition state conversion rate. This unit difference manifests in the phenomenological rate constant having a scaling factor relative to the intrinsic rate constant due to different units in $[A]^\circ$ and $[TS]^\circ$. In practice, this affects the pre-exponential and the entropy of activation. As it may not be practical for all users to account for this factor, simply stating the elementary step and type of transition state assumed and using common units across studies will make any ‘errors’ systematic, allowing entropies of activation to be directly comparable. Standardization will also facilitate the obtaining of truly intrinsic values by specialists later.

Table 5.1: Summary of standard entropy of activation values using data from a few recent studies in corrosion. Column headers indicate the units of the rate used in calculating the standard entropy of activation values (first header), and the value of the standard state of the surface (second header) listed in the table. Bolded numbers represent the reported entropies in the reference article with other numbers in that row based on transformations to the relevant unit systems. Transformations between Coulomb-based and mass or thickness based systems assumed a final metallic charge state of +3 from 0 (i.e., a 3 electron transfer reaction). Comparison of these reported values to those calculated using the recommended system is given in Table 5.3.

[Ref] System	Solutes added to the system	Standard Entropy of Activation, $\Delta^\ddagger S^\circ$ (J/mol K) From Reaction Rates in First Header Row, and Implied Surface Standard State in the Second Header Row						
		$\frac{A}{cm^2}$	$\frac{mA}{cm^2}$	$\frac{\mu A}{cm^2}$	$\frac{A}{m^2}$	$\frac{mm}{yr}$	$\frac{mg}{cm^2 s}$	$\frac{mg}{cm^2 h}$
		$1 \frac{C}{cm^2}$	$1 \frac{mC}{cm^2}$	$1 \frac{\mu C}{cm^2}$	$1 \frac{C}{m^2}$	1 mm	$1 \frac{mg}{cm^2}$	$1 \frac{mg}{cm^2}$
[185] Steel exposed in 15% HCl	Blank	-126	-183	-241	-203	-200	-112	-180
	10 ⁻³ M Inhibitor 1	-96	-153	-211	-173	-170	-82	-150
	10 ⁻³ M Inhibitor 2	-159	-216	-274	-236	-233	-145	-213
[186] Aluminum/SiC composite	0.025 M HCl	50	-7	-65	-26	-102	-5.7	-74
	0.1 M HCl	126	68	11	49	-27	70	1.8
	0.25 M HCl	35	-23	-80	-42	-118	-21	-89
	0 wt% NaCl	78	21	-37	2	0.91	89	21
[187] 43035 SS exposed in 2 M H ₂ SO ₄	1 wt% NaCl	83	25	-32	6	5.4	93	25
	3.5 wt% NaCl	82	25	-32	6	5.2	93	25
	6 wt% NaCl	84	26	-31	7	6.5	95	26
[188] Carbon steel exposed to 1 M HCl	Blank	18	-39	-97	-58	-56	32	-36
	10 ⁻³ M PTB	33	-24	-81	-43	-41	47	-21
	10 ⁻³ M DTB	55	-2.2	-60	-21	-19	69	0.8
[189] Carbon steel exposed to 1 M HCl	Blank	-93	-151	-208	-170	-168	-79	-148
	10 ⁻³ M SMQ	11	-47	-104	-66	-64	25	-44
	10 ⁻³ M TMQ	-29	-87	-144	-106	-104	-16	-84
[190] Steel exposed to 1 M HCl	Blank	-142	-199	-257	-218	-216	-128	-196
	0.2 M META	-128	-185	-243	-204	-202	-114	-182

Table 5.2: Summary of standard entropy of activation values using data from three recent studies in catalysis. The column headers indicate the units of the rate used in calculating the standard entropy of activation values listed in the table. Bolded numbers indicate the reported numbers by the reference article, other numbers in that row are based on transformations to the other relevant unit systems. These values are compared to the system recommended by the authors in Table 5.3.

<i>[Ref]</i> <i>System</i>	<i>Catalyst</i>	<i>Calculated Standard Entropy of Activation (J/mol K)</i> <i>with Reaction Rates in Units Given in Headers</i>			
		$\frac{1}{min}$	$\frac{1}{sec}$	$\frac{1}{hr}$	$\frac{1}{yr}$
<i>[191]</i> <i>Biodiesel production</i>	Spirulina platensis	-233	-199	-267	-343
	Chlorella	-180	-146	-214	-290
	Leather tanning waste	-233	-199	-267	-343
<i>[192] Cracking of pentane</i>	I-SBAS	-29	5	-63	-139
	EFAI-SBAS	24	58	-10	-86

to reflect a case where there is a surface adsorbate reactant going to surface transition state, or a surface species (such as a site) changing states such that the reactant and transition state are again both surface states. In this case, the activity is given by the extent of coverage, which is assumed to be proportional to the rate. As justified in the next section, such an assumption is likely valid for many corrosion systems.

Table 5.1 and Table 5.2 list the reported standard entropy of activation values (bolded numbers) along with what the standard entropy of activation is if adjusting to various arbitrary other standard state choices (see column headers). The values for the standard states recommended in this work are not shown in Table 5.1 and Table 5.2, but will be shown in the next section. The adjustment between columns (that is, between standard state choices) was made by noting that transformations between standard states involves adjustment of the C° term. As a second issue, failure to correctly cancel the time units (while using a typical value for the $k_B T$ term) can have a significant impact on the predicted standard entropy of activation, as this would be equivalent to adding an additional coefficient to the C° . Including the effects of such time units, differing implied standard states for the C° , and taking the activity coefficients to be one, Eqn. 5.9 becomes,

$$\Delta^\ddagger S^\circ_{table} = R \left[b + \ln \left(\frac{C^\circ_{reported} h}{C^\circ_{reported} C^\circ_{table} u_{t,reported} k_B} \right) - 1 + \frac{P \Delta^\ddagger V^\circ}{RT} \right] \quad \text{Eqn. 5.13}$$

Where the variables are as defined below Eqn. 5.3 and Eqn. 5.9 and where $u_{t,reported}$ is the unit of time initially reported, as converted to seconds (e.g., $u_{t,reported} = 60 \text{ s}$ when the reported unit of time is minutes). The underscores “reported”, and “table” refer to the values reported (or implied) in the relevant papers and corresponding values in the table, respectively. Simplification of Eqn. 5.13 provides the conversion equation,

$$\Delta^\ddagger S^\circ_{table} = \Delta^\ddagger S^\circ_{reported} + R \ln \left(\frac{C^\circ_{reported}}{C^\circ_{table} u_{t,reported}} \right) \quad \text{Eqn. 5.14}$$

For example, switching from rate units of $\mu\text{A}/\text{cm}^2$ to mA/cm^2 requires multiplication by 10^{-3} , resulting in an increase in the calculated standard entropy of activation term by $57 \frac{\text{J}}{\text{mol K}}$, as reflected in the table for relevant studies. Transferring between mass or thickness change and current requires an assumption about the ionization reaction mechanism. In the present work, all ionization reactions were assumed to undergo a transfer of 3 electrons. While not all-inclusive of active electrochemical mechanisms, this assumption is a reasonable approximation for demonstrative purposes⁸. To evaluate the impact on the result, transfer of only 1 electron

⁸ For example, converting between columns 1 and 6 is done with, $\frac{C^\circ_{\text{A}/\text{cm}^2}}{C^\circ_{\text{mg}/\text{cm}^2\text{s}}} = \frac{F n_e}{1000 MM_{\text{surface}}}$, where MM_{surface} is the molar mass of the surface (g/mol surface), F is the Faraday constant ($9.6485 \times 10^4 \text{ C/mol electrons}$), n_e is the number of electrons transferred in the reaction (or the mol e^- /mol rxn), and the factor of 1000 converts the result in mg from g. The units of this factor are C/mg, which is required to convert the rate constant from a standard state of $1 \text{ C}/\text{cm}^2$ to $1 \text{ mg}/\text{cm}^2$.

decreases the calculated values by about 10 J/mol K, while a transfer of 5 electrons increases it by about 5 J/mol K. For the second and third entries, of Table 5.1, the cited articles presented a more accurate electrochemical conversion specific to their system, and those reported conversions were used in place of the three-electron assumption.

In looking at Table 5.1 and Table 5.2, these studies differ in how the reaction rate of the surface was reported (bolded column of table), which is related to the implicit definition of the surface species standard state, as noted earlier. Thus, comparison between studies involves shifting between standard states of the surface species. Unless there is reason to believe the surface is less than fully active, the standard state should always correspond to unit activity (a method for this is described in the next section). As an example, for rate constant units of $\text{mg cm}^{-2} \text{s}^{-1}$ the implied standard state (if one is not specified and accounted for) is 1 mg cm^{-2} which requires that 1 mg of the surface per cm^2 would be available to react in the standard state. This can be converted to a fraction of the surface exposed to the reactants. For example, Fe at room temperature with an activity of 1 and the first unit cell available to react (2 atoms/unit cell) contains $2 \times 10^{-4} \text{ mg cm}^{-2}$, significantly less than 1. Therefore, the standard state of 1 mg cm^{-2} is not only hypothetical but also non-physical. A similar issue occurs for other states in Table 5.1, and this motivates the need to use the standardization described in the next section.

Additionally, as noted above, the authors recommend following the CODATA recommendation of using rates with seconds as the unit of time. This is because the elementary step pre-exponential is usually in the SI units of s^{-1} , and failure to correctly cancel the time units can have a significant impact on the predicted standard entropy of activation, as this would be equivalent to adding an additional coefficient to the C° term. This difference is demonstrated notably by Table 5.2. Thus, s^{-1} should be used, or conversions to seconds explicitly included in the calculation of entropy.

Despite the afore-mentioned potential for difficulties in comparing studies with different explicitly or implicitly defined standard states, the standard state conversions do not typically result in changing the sign of the standard entropy of activation. However, as the tables show, some sign changes do occur following certain unit transformations. As the various standard states can be non-physical (more material required than available to react) or correspond to deactivation of parts of the surface (activity less than 1), the reasonableness of obtained standard entropies of activation is difficult to assess unless the community adopts greater standardization.

5.6 Proposal of Standard to Report Data and Discussion of Limitations

5.6.1 The Surface Reactant Equi-density Approximation (SREA) Method

To facilitate comparisons between reaction systems and provide for appropriate representation of unit activity surfaces, a standard for evaluation of reactions with a surface is herein proposed. It is the authors' desire that this proposal will begin a discussion to more rigorously apply TST to experimental systems. The proposed standard is based on conversion of solution concentrations of reactants to molecular ratios with the surface (including the surface itself), which is equivalent to a fractional coverage standard state of 1 (or $c_{\text{ads}}^\circ = \theta_{\text{ads}}^\circ = 1$). When sufficient information

is available about how the surface species concentration scales with solute concentration (or gas phase pressure), the Langmuir isotherm, microkinetic modeling, or other methods can be used to estimate the surface species concentration.

In the absence of such knowledge, for corrosion science it can be assumed that in many cases the active species is a surface state that is of low surface concentration and in a pre-equilibrium with the solute molecules (or gas phase molecules) in the fluid phase⁹. In this case, there will be a surface species that converts to a surface transition state, and the surface species will be proportional in concentration to the fluid phase concentration of the solute (or gas phase molecule). In such cases, an equi-density approximation can be applied between the surface phase and the solution phase in order to obtain a standardized activity scale between experiments taken at different concentrations. While this does introduce error, such error will be mitigated for two reasons: a) adsorption often involves a small change in Gibbs energy, and thus the temperature dependence of the error will be relatively small compared to that of the activation energy, b) any error introduced from the equi-density approximation will appear inside the natural log term of Eqn. 5.13, and will at least allow comparison between different studies. It is important that the equi-density approximation be clearly stated when used, as later researchers can then backwards-correct an individual study's results to be more accurate if further information is later obtained. To accomplish the equi-density approximation practically, a volume of solution (or gas) is considered with a unit cross-sectional area and a depth of a single molecular layer, with all reactants assumed to be well-mixed. This is similar to the concepts used in defining a Gibbs dividing surface [193-201]. Concentrations of component molecules are then converted to areal densities and divided by the areal density of the active surface to determine fractional active-surface concentrations. This approximation is only appropriate to use when the reaction rate is observed to be proportional to a solute (or gas phase molecule): when there is no dependence on the fluid phase concentration, it should be assumed that there is an activity of 1 over the entire surface or some percentage of the surface.

The areal densities may be determined relative to active sites (units of rtL) by experimental evaluation (such as in Xie et al [202] through chemisorption of CO). Otherwise, a simple geometric assessment (units of rtG) can be accomplished by averaging presented molecular surface densities over various crystal orientations with the assumption of full surface activity. While this latter approach is unideal, it is a useful approximation in cases where evaluation of specific surface activity is not possible, or extremely difficult. For example, corrosion in high pressure, high temperature liquid water presents a challenging environment for such evaluations. For porous materials, a geometric assessment may be insufficient, requiring experimental methods that can probe the accessible area, such as by the Brunauer-Emmett-Teller model and possibly considering the fractal area [203]. The areal densities of the component concentrations,

⁹This picture also assumes that there is an elementary step which has a high degree of rate control a single atom or an ensemble of atoms at the surface changing bonding or re-arranging. In this case, the elementary step is a unimolecular surface species rearrangement (occurring within that ensemble of atoms, which can be treated as an 'embedded molecule' within the surface) and the transition state is also a surface species (effectively, the rest of the surface is like a solvation environment around that ensemble of atoms).

S_i , could then be divided by the areal density of the substrate, S_u , providing concentrations in units of mol S_i per mol S_u .

A general calculation to accomplish this concentration conversion is provided below in Eqn. 5.15 for reactions in a fluid. Similar equations can be developed for gases.

$$\theta_{S_i} = [S_i] \left(\frac{MM_{m,solvent}}{N_{av}\rho_{solvent}} \right)^{\frac{1}{3}} \left(\frac{a_o^2 N_{av}}{n_{Su}X} \right) \quad \text{Eqn. 5.15}$$

Where, θ_{S_i} is the fractional concentration in rtL units for the i^{th} solute (S_i) in mol per mol of active surface molecules (S_u), $[S_i]$ is the concentration of solute S_i in mol/dm³, $\rho_{solvent}$ is the density of the solvent in g/dm³, $MM_{m,solvent}$ is the molar mass of the solvent in g/mol, n_{Su} is the average number of surface atoms exposed to the solution per unit cell with lattice constant of a_o in dm², X is the fraction of surface species that are active (set to 1 if unknown), and N_{av} is Avogadro's number. In Eqn. 5.15 the first term is the concentration in solution, the second term describes the depth of the chosen volume, and the third term describes the inverse of the areal density of the active surface molecules. Eqn. 5.15 rearranges to Eqn. 5.16, which may be used generally in experimental studies.

$$\theta_{S_i} = \frac{[S_i]a_o^2}{n_{Su}X} \left(\frac{MM_{m,solvent}N_{av}^2}{\rho_{solvent}} \right)^{\frac{1}{3}} \quad \text{Eqn. 5.16.}$$

Thus, the final rate can then be expressed as corresponding to a single elementary step molecular surface species reaction,

$$Rate = Ae^{-\frac{E_a}{RT}} \prod_i^m \theta_i^{n_i} \quad \text{Eqn. 5.17}$$

Where n_i is the reaction order of reactant i , m is the total number of reactants, and $Rate$ is the reaction rate in inverse seconds. For both catalysis and corrosion, this corresponds to the number of reactions occurring per surface sites available to react.

For corrosion with linear mass change, the experimental rate is commonly expressed as a mass change per surface area, with units similar to mg/cm²s. In this system, the $Rate$ term in Eqn. 5.17 with units of mol reacted per mol surface per second is obtained by,

$$Rate = \frac{0.1 a_o^2 MM_{m,Su}}{n_{Su}X} Rate_{exp} \quad \text{Eqn. 5.18}$$

Where $Rate_{exp}$ is the rate in its original units of mg/cm²s, MM_{Su} is the molar mass of the surface, and the other terms are as previously defined. The rate can be reduced to the following general form by defining a conversion factor, C_t , which takes the units and value needed to convert from any experimental unit system to the SREA method.

$$Rate = C_t Rate_{exp} \quad \text{Eqn. 5.19}$$

Compiling these equations for systems with reacting component concentrations initially defined in mol/L concentrations without specifying the units of the rate, and assuming unit activity coefficients and standard states,

$$C_t Rate_{exp} = \frac{k_B T}{h} e^{\frac{\Delta^\ddagger S^\circ}{R} + 1 - \frac{P\Delta^\ddagger V^\circ}{RT}} e^{-\frac{E_a}{RT}} \prod_i^m \left[\frac{[S_i] a_o^2}{n_{su} X} \left(\frac{\rho_{solvent} N_{av}^2}{MM_{solvent}} \right)^{\frac{1}{3}} \right]^{n_i} \quad \text{Eqn. 5.20}$$

In order to plot $\ln(Rate)$ as a function of $1/T$, Eqn. 5.20 can be expressed as Eqn. 5.20,

$$\ln \left(\frac{C_t Rate_{exp} u_T}{T \prod_i^m \theta_{S_i}} \right) = \ln \left(\frac{C_t Rate_{exp} u_T}{T \prod_i^m \left[\frac{[S_i] a_o^2}{n_{su} X} \left(\frac{\rho_{solvent} N_{av}^2}{MM_{solvent}} \right)^{\frac{1}{3}} \right]^{n_i}} \right) \quad \text{Eqn. 5.21}$$

$$= \left[\ln \left(\frac{C^\circ k_B u_t}{h} \right) + \frac{\Delta^\ddagger S^\circ}{R} + 1 - \frac{P\Delta^\ddagger V^\circ}{RT} \right] - \frac{E_a}{RT}$$

Plotting Eqn. 5.21 as either version of the term including the rate versus $1/T$ allows a linear fit and the intercept, **b**, can be related to the entropy of activation as previously described with Eqn. 5.21. Naturally, where surface coverage is known, that value should be used for concentrations from the SREA method in the Π term. Additionally, these approximations are of course not a complete substitute for a more thorough microkinetic model which would consider all elementary steps. However, these approximations are a practical method for comparing values between systems in the absence of complete chemical reaction network kinetics information. Thus, they represent a practical compromise between efficiency and improved chemical knowledge for corrosion science.

5.6.2 Discussion of Limitations and Application to Reported Data

Since the surface activity is accounted for, the primary limitation in this method relates to its introduction of error in the determination of the surface concentrations of relevant solutes. The error is introduced by using an equi-density approximation between the areal densities of the reactants are in the bulk and those at the surface, as demonstrated by Eqn. 5.15. Especially in polar liquids, the concentrations at the surface/liquid interface may not be equal to those in the bulk due to the altered chemical environment within an interaction layer of the surface caused by the chemical forces from the surface, and re-organization of the liquid near the surface. Additionally, at high concentration the surface coverage will approach the thermodynamic saturation and no longer correlate simply to the concentration in the bulk (see section 5.2). This will be further exacerbated if the surface sites are polar (such as with many ceramics).

Effectively, this convolves the effects of adsorption with reactions on the surface. Where adsorption has a high degree of rate control, this assumption does not affect the accuracy. However, when adsorption does not have a high degree of rate control, for example due to a lack of pre-equilibrium, the surface coverage would be beneficial to assess, such as by FTIR or other methods [192, 202]. Lack of any dependence on the fluid phase concentration would suggest an activity of 1.

As an illustration of the effect of applying this model, it was applied to the data in Table 5.1 and Table 5.2 to convert the entropies to the standards recommended in this work. The results are shown in Table 5.3. The data in the first column are the numbers in bold in the former tables, the second column contains adjusted values, and the third column represents the difference.

For systems exposed to HCl or H₂SO₄, the acid concentration was not considered in the correction due to the lack of an explicit chemical model applied in the relevant works (i.e., it was treated here like a catalyst for corrosion in the sense of lowering the activation energy, but not in the sense of having an activity in the rate equation). For inhibited corrosion reactions, a single adjustment method is not obvious since inhibitors fall into a variety of categories [185]. The studies referenced below indicated the inhibitors impacted the chemical adsorption properties of the corrosive molecules, affecting the corrosion mechanism. Additionally, the surface coverage of many systems where the TST analysis was conducted was near 100%. Thus, in the inhibition studies, the effect of chemical concentration was not considered.

These applications demonstrate an additional limitation of the method. As it requires a specific chemical system, it is ideally suited to conditions where chemical reactions are well known and separable. For example, the high temperature aqueous corrosion of SiC can be divided into eight reactions [11, 14, 89, 204] which can be at least partly separated through detailed investigation. In such cases, the reactant concentrations can be readily accounted for. Even in these circumstances, the method presented here will only be accurate if there is a single step that has a high degree of rate control. Otherwise, the resulting activation parameters will represent an aggregate of all steps with a non-negligible degree of rate control. This highlights an additional potential benefit of applying TST in the absence of a full microkinetic model: for cases where a mechanism is quite complicated, the observed entropy of activation when approximating an apparent rate constant as that of an elementary step will no longer correspond to a single reaction step in a mechanism, and unrealistic values can *themselves* provide insight into the complexity of an observed process by virtue of their unrealistic magnitudes.

As shown in Table 5.3, the effects of applying this proposed recommendation range widely depending on the system compared. The first entry in the table represents a catalysis system where a similar method was applied, resulting in no improvement from the present method. As a result of the unit choice, the studies by Kahled et al [190] and Sebhaoui et al [188] happened to also have no substantial change in the value. The other studies saw sharp changes, most of which resulting in an increase in the standard entropy of activation when applying the present recommendation.

Table 5.3: Evaluation of the standard entropy of activation of the reaction systems from Table 5.1 using the SREA method, with the original reported entropy also listed. To construct this table the standard state of the surface was converted as described above, and the unit of time was converted to seconds. The solute components were not considered in the equi-density approximation for the conversion due to explicit chemical systems not being set forth, or due to it already being included by the study.

[Ref] System	Solutes added to the system/ reaction catalysts	Calculated Standard Entropy of Activation (J/mol K)		
		Reported Value	Value Using SREA Method	Difference
[185] Steel exposed in 15% HCl	Blank	-126	-191	
	10 ⁻³ M Inhibitor 1	-96	-161	-65
	10 ⁻³ M Inhibitor 2	-159	-224	
[186] Aluminum/SiC composite	0.025 M HCl	-102	-87	
	0.1 M HCl	-27	-12	15
	0.25 M HCl	-118	-103	
[187] 43035 SS exposed in 2 M H₂SO₄	0 wt% NaCl	0.91	19	
	1 wt% NaCl	5.4	24	
	3.5 wt% NaCl	5.2	23	18
	6 wt% NaCl	6.5	25	
[188] Carbon steel exposed to 1 M HCl	Blank	-39	-47	
	10 ⁻³ M PTB	-24	-32	-8
	10 ⁻³ M DTB	-2.2	-10	
[189] Carbon steel exposed to 1 M HCl	Blank	-208	-158	
	10 ⁻³ M SMQ	-104	-54	50
	10 ⁻³ M TMQ	-144	-95	
[190] Steel exposed to 1 M HCl	Blank	-196	-198	
	0.2 M META	-182	-184	2
[191] Biodiesel production	Spirulina platensis	-233	-199	
	Chlorella	-180	-146	
	Leather tanning waste	-233	-199	34
[192] Cracking of pentane using zeolites	I-SBAS	5	5	
	EFAl-SBAS	58	58	0

These differences are visually shown in Figure 5.1 as a difference in calculated entropy relative to the SREA framework set forth in this work. Conversion between units assumed a reaction of Fe ionizing to Fe^{3+} with $\kappa = 1$. Several points are useful to note from this figure. First, even large deviations in κ result in rather small errors in the calculated entropy regardless of unit choice. Thus, while knowing κ is useful, the error in choosing an incorrect κ is small relative to other errors (especially choosing certain unit systems). Second, deviations as large as 80 J/mol K are seen between certain choices of units (that is, implied standard states), while they are nearly zero for others. This highlights the importance of setting a standard evaluation method, such as set forth here, so that practitioners do not need to worry about ‘implied’ standard states. Third, while some commonly used units appear to give an identical result to the SREA method, this is an artifact of the chemical system chosen for comparison ($\text{Fe} = \text{Fe}^{3+} + 3\text{e}^-$). Choice of a different system, such as $\text{Na} = \text{Na}^+ + \text{e}^-$, can increase the differences of those units by 20 J/mol.

5.7 Summary

Transition state theory (TST) is a powerful tool for the evaluation of chemical systems through an estimate of the standard entropy of activation to form the activated complex, with the standard enthalpy of activation being close to the activation energy from the Arrhenius equation. A lack of uniformity in calculation of the thermodynamic values of activation has led to the publication of studies with difficult-to-compare standard entropies of activation (and has also increased the chances of inaccurate reporting). To address this challenge, recommendations that better align with existing standards are proposed, with specific guidelines provided, including an application method for empirical data analysis that can be widely applied. The goal is to increase the scientific rigor of standard entropy of activation estimations for reactions occurring on or with a surface. Part of this proposal involves the normalization of all rates and reactant concentrations to available surface molecules, with a surface reactant equi-density approximation (SREA) when additional information is not available. Application of the recommendations consistently across different results to put them on a common scale has been shown in this work to adjust entropy of activation values by offsets ranging from -65 to 50 J/mol K relative to the originally reported values. The impact of the recommendations is thus significant for comparing values between systems and attempting to understand the meaning of the values. This method is applied to the evaluation of SiC corrosion kinetics in the following chapter.

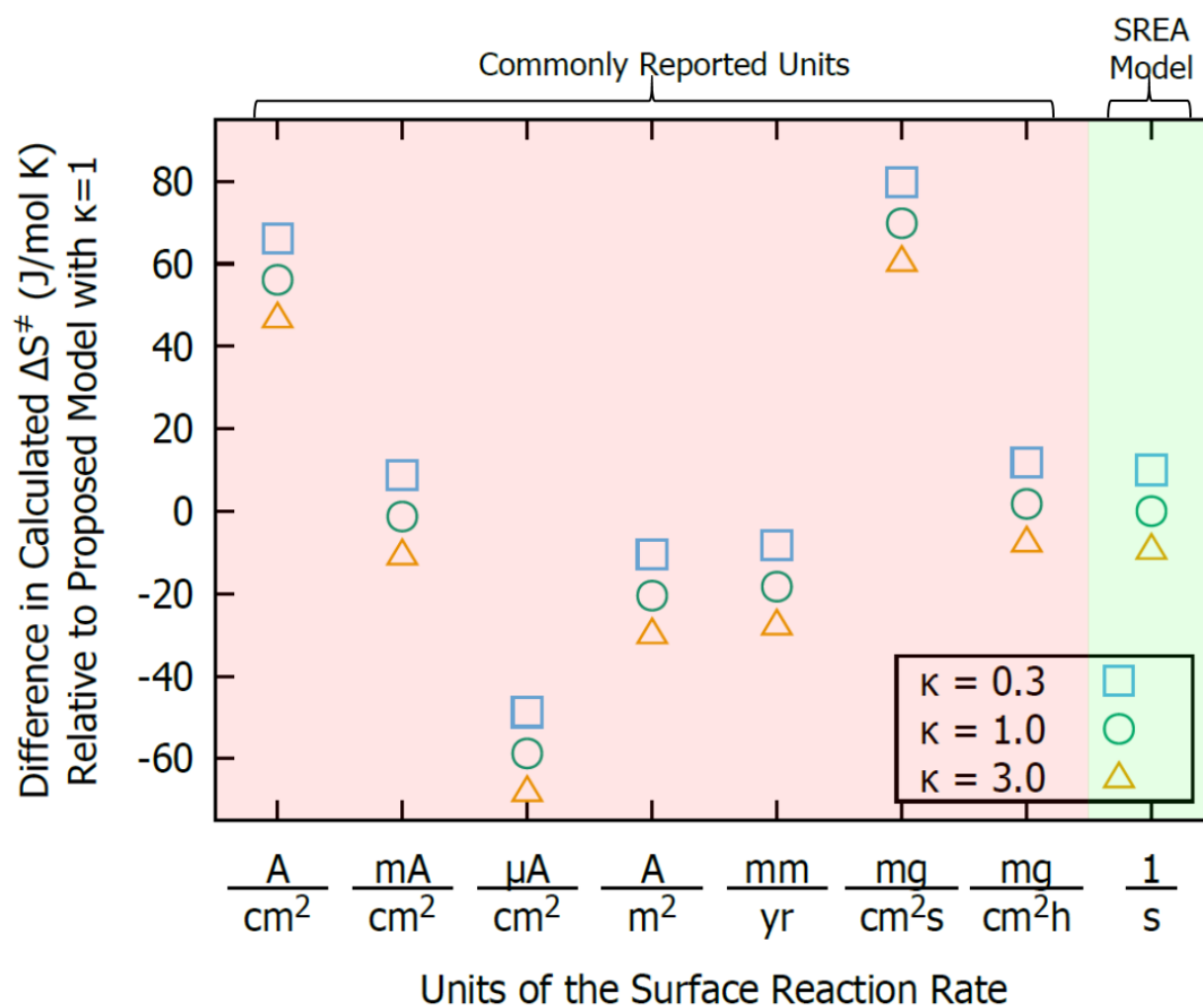


Figure 5.1 Comparison of the effect of the reaction rate units on calculated standard entropy of activation for the reaction of $\text{Fe} = \text{Fe}^{3+} + 3\text{e}^-$. The proposed model is shown on the right with severally commonly used units on the rest of the plot. The values in the figure represent a deviation in reported entropy from using the proposed model with $\kappa = 1$. Squares represent a diminished transmission coefficient, $\kappa = 0.3$; circles represent $\kappa = 1$, and triangles represent enhanced transmission of $\kappa = 3$.

Chapter 6: Analysis and Discussion

6.1 Assumed Acceptable Corrosion Behavior for SiC

Intended designs of SiC-based nuclear fuel cladding use SiC/SiC CMCs to compensate for the brittleness of monolithic SiC and to provide higher strength for the expected stresses involved. CMC's may be built with two or three sections. A SiC monolith, several hundred micrometers thick, may be present to serve as a diffusion barrier, although this has problematic implications for stress distributions in-service [20]. The stress-carrying portion of the CMC consists of the fiber preform infiltrated with a matrix. A final coating of CVD SiC, at least 50-100 μm thick, covers the woven fibers and serves as a diffusion barrier and a sealant against the environment [11, 205, 206]. Given the recent modelling work indicating likely bowing with extensive stress concentrations of SiC-based cladding and channel boxes in BWR flow channels [207, 208], maintaining the strength of this cladding is essential. However, the vital PyC fiber-matrix interfaces can be degraded by exposure to high-temperature water [23, 52, 209, 210].

The current regulatory standard for fuel cladding in the U.S. is based on the metallic Zr-based alloys, and limits cladding thickness loss to 17% of the original thickness (10 CFR § 50.46). This standard is not relevant for SiC-based tubes as they are not monolithic; the final standard will be determined by the relevant regulatory agencies. In the present work, the authors assume that the outer SiC monolith must be retained. This translates to a maximum thickness loss of 50 μm by the end of cladding life (about 5 years). This chosen standard is admittedly somewhat arbitrary, and given the possibility of outer monolith cracking, corrosion should be minimized to well below the full thickness of the outer monolith.

6.2 Implications of the Scoping Test Data Regarding Alumina, Silica, SiC, and the Down-selection of Coatings

The rapidity of the corrosion of Si and SiO_2 confirms previous results [11] and together with the chemical equations in section 2.9.1 suggests the SiC reaction with water is the rate-limiting step in its corrosion. If SiO_2 dissolved at a similar rate to SiC, then the rate limiting step would be the dissolution of SiO_2 after the SiC reacts with water. The chemical kinetics of the SiC corrosion reaction are discussed in section 6.3.1.

6.2.1 Alumina Corrosion Characteristics

As shown in Figure 4.1, polycrystalline alumina degraded significantly more quickly than single crystal alumina. This suggests a pronounced effect of grain boundaries on the dissolution. Figure 4.1a shows polycrystalline Al_2O_3 corrodes at rates such that $\text{BWR-HWC} > \text{PWR} > \text{BWR-NWC}$ conditions. Figure 4.1b shows the single crystalline variety corroding with the same trend, but at noticeably lower rates than Figure 4.1a (between approximately 1.3 and 1.5 times). This behavior can be explained by some of the surface features in Figure 4.2 and Figure 4.3 which reveal significant attack of grain boundaries with otherwise uniform attack of the surface.

The images in Figure 4.2 show no indication of localized corrosion and any deviations from uniform corrosion would be caused by localized chemistry, which typically is exacerbated by rough surfaces, crevices, etc., none of which are apparent in these images. Figure 4.3 shows low

magnification images of polycrystalline alumina exposed to each of the three water chemistries. These are also indistinguishable, and each sample shows clearly protruding regions of alumina that appear to be individual grains. One mechanism for this to occur is by selective attack of the grain boundaries, causing fallout of grains surrounding the ones observed. This would lead to the very rough structure observed in this work. It is thus suggested that uniform corrosion of grain surfaces is combined with selective attack of grain boundaries leading to grain fallout. In the absence of grain boundaries, alumina degrades more uniformly. The mass change observation that polycrystalline samples corroded significantly faster than the single crystal samples is consistent with this hypothesis.

The differences in Raman spectra of single and polycrystalline alumina in Figure 4.4 may be caused by grain boundary stresses altering the chemical environment of the Al_2O_3 in the vicinity of those boundaries, or by dangling bonds at the boundaries, such as observed in [97]. The heterogeneous diaspore distribution over the surface of the polycrystalline alumina sample exposed in NWC water may be because of either some mineral-to-mineral transformation under these conditions, or some dissolving Al_2O_3 subsequently redeposits as $AlO(OH)$. Of these possibilities the latter is considered the most likely since $AlO(OH)$ has been shown to have a significantly lower equilibrium constant for dissolution than Al_2O_3 and $AlO(OH)$ typically transforms into Al_2O_3 slowly over time, rather than the reverse due to significant differences in the Gibb's free energy of formation [211, 212]. However, this makes the deposition of $AlO(OH)$ surprising due to its greater thermodynamic instability. It may be that the flowrate of water through the system may have been slow enough that sufficient Al^{3+} builds up to precipitate out $AlO(OH)$, whereas not enough builds up to deposit Al_2O_3 . This may account, in part, for the low corrosion rate in the NWC condition, and possibly PWR, relative to the HWC condition. However, this explanation would lead to the expectation of $AlO(OH)$ on the single crystal specimens as well, which was not observed.

As a rough kinetics analysis, Al_2O_3 was assumed to dissolve by the following equation and rate constant, neglecting re-deposition. For this simplistic analysis, linear kinetics were also assumed, despite the above discussion.



While there are many other possible equations of dissolution, the listed equation was assumed to be dominant due to the relative abundance of water compared to its self-ions. Assuming unit activities of water and the alumina specimen, the rate is simply equal to the rate constant, K , with units of $mg/cm^2 \cdot s$. For polycrystalline specimens, $K_{NWC,P} = 1.5 \times 10^{-6}$, $K_{HWC,P} = 2.8 \times 10^{-6}$, $K_{PWR,P} = 1.8 \times 10^{-6}$. For the single crystalline specimens, $K_{NWC,S} = 1.0 \times 10^{-6}$, $K_{HWC,S} = 2.0 \times 10^{-6}$, $K_{PWR,S} = 1.5 \times 10^{-6}$.

In summary, alumina degrades by simple dissolution with enhanced grain boundary attack. Even without grain fallout, in 5 years the smallest expected thickness recession would be 0.5 mm in an NWC environment, which is unacceptable. As alumina is currently a required component of

sintered SiC this will yield an unacceptable corrosion rate as previously observed for NITE SiC [15], necessitating the use of a CVD SiC overcoat with or without corrosion/hermeticity coatings, which is the focus of the present work.

6.2.2 SiC Corrosion Characteristics

In the following comparisons of the SiC corrosion rates represented in Figure 4.5, it should be noted that the mass-loss-per-area numbers reported were obtained for extremely low true mass losses (on the order of hundredths to tenths of a mg for most samples and up to a few mg for the most corroded (LR, NWC) sample). Coupled with the fact that only one sample was used for each condition, these trends should be seen as approximate trends rather than exact kinetic representations, which are dealt with more robustly in section 6.3.

Several points fall out of the data observations given in section 4.1.3. First, no SiO₂ was observed on any SiC surface using Raman spectroscopy. This is in agreement with the observed rapid loss of material Si and SiO₂ in the presence of hot water (section 4.1.1) and with previously reported data [11] and has the significance of implying that SiC corrodes without passivation. In Figure 4.10d for the NWC case, the unmarked peaks do not align with any Si, SiO₂, or SiC peaks and thus are likely to be from metal oxide contaminants that deposited on the surface of the specimen.

Second, in the HWC environment, all the samples degrade at effectively the same low rate with an approximate 5 year thickness loss of ~2.5 μm , well below the threshold for concern. However, the error is quite high in part due to only one sample of each type being exposed, and in part due to the low mass loss signal. Third, in the PWR exposure, no conclusions regarding the reaction rate can be made. All the mass losses were observed to be parabolic, which is not consistent with previous data or with the lack of observation of any SiO₂ on the surface. It is possible that the samples were damaged during the sample handling process after the first month, and the apparent parabolic behavior could be a result of this hypothesized handling artifact combined with data scatter in the subsequent tests.

Fourth, unlike the alumina specimens, there is no indication that grain boundaries of high resistivity SiC are highly susceptible to corrosion. While some likely grain boundary attack was observed (Figure 4.9), it was not significant enough to show up in the mass loss. It should be noted that the 4H sample, while having a lower overall mass loss in the NWC environment, behaved identically to the high resistivity samples in the first and third exposure segments. Especially in light of the lack of extensive grain boundary attack or significant fallout being likely, the second exposure likely involved some handling error resulting in the observed discrepancy. Finally, while the low resistivity sample was similar to the others in HWC, extensive grain fallout resulted in dramatic and superlinear mass loss over the course of the NWC exposure, as best illustrated by the micrographs in Figure 4.6. This is in agreement with a recent study at higher temperature [100]. The consequence of this is a potential need to provide additional protection of lower resistivity SiC in NWC water chemistry reactors. Further analysis is reserved for section 6.3.1 and following.

6.2.3 ORNL HCL Coatings Scoping tests

The scoping tests were used to down-select coatings for further evaluation. As clearly shown in Figure 4.11 and Figure 4.13, both the ZrN and NiCr spalled significantly. On this basis they were removed from additional testing. The NiCr coating was produced using of electroless deposition which is significantly more scalable than the more established PVD, and also significantly cheaper due to the room temperature deposition and the liquid-phase medium. Further, additional coatings can then be electrodeposited on top of the Ni or NiCr first layer. However, since this coating was not ready for further evaluation, it was removed from further study in this work and will hopefully be more fully developed at a future point. Additionally, the pure Ni was removed from further testing due to high neutron absorption cross sections. The scoping tests confirm that a Ni coating can be both adherent and protective and thus could be used a compatibility layer for the brittle ceramic coatings, as in the MITR exposures discussed in section 6.6.

In both conditions, the TiN gained mass in a roughly parabolic fashion. This is expected according to reactions forming TiO_2 , which is stable in both sets of environments. Following initial mass gain, potential mass loss begins in the HWC environment, which may indicate a spallation risk in the long term. The significantly greater mass change of the solid TiN compared to the coating is due to the fact that the solid sample was a highly porous sintered material, and thus only partially represented the coating material. As such, it was removed from future tests.

The CrN samples did not perform well in either condition, losing mass in both. While CrN should form Cr_2O_3 to protect it from corrosion, the loss of material suggests potential coating instability. However, since only one sample of each was included, and the CrN did not immediately spall from the SiC, it was retained for the subsequent tests, with details given in Chapter 3.

The lack of substantial mass change in either HWC or NWC suggest potential stability of the Cr coating over the longer term. In NWC, the solid Cr appeared to lose some mass, indicating a potentially rapid dissolution of Cr_2O_3 into the coolant. Chemical reactions and stability of the various expected and observed coating reaction products and kinetics are discussed at greater length in section 6.5 where more data allows more useful conclusions.

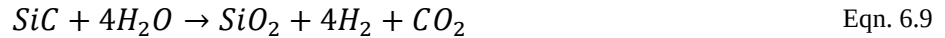
As with the GE tests, the CVD SiC degraded rather slowly in the HWC tests from this study and thus are not conclusive given the error and short test times. In NWC water chemistry, the samples did not appear to degrade significantly over 400h, as expected from the GE tests in this work. In contrast, the CMC SiC lost substantial mass. This is likely related to the exposure of fibers and fiber-matrix-interphases to the water environment either due to cracking of the external monolith or due to the cutting of the samples following a CVD overcoat, and thus exposing the interiors. The latter of these is most likely also the cause of the Cr coating on CMC SiC losing substantial mass. Following cutting, the deposition of Cr would lead to Cr directly coated on fibers and PyC interphases, rather than on the monolithic CVD SiC overcoat on the fibers. Such deposits may not be as adherent as a uniform layer and could be removed if the PyC interphases on the fibers were selectively attacked, if the fibers themselves were removed by corrosion of exposed interphases, or by simple spallation due to poor coating. As this effect is not likely to be relevant to industrial applications (a CMC SiC rod will always be fully coated

with monolithic CVD SiC prior to coating deposition) and because this thesis is focused on a more fundamental understanding of SiC corrosion, the topic of CMC SiC was not explored further in the autoclave experiments, but some CMC Si coupons were included in the MITR exposures.

6.3 Exposures of Uncoated SiC in the Absence of Irradiation at ORNL

6.3.1 Corrosion Kinetics Evaluation

The eight reactions of SiC with water and oxygen given in section 2.9.1 are reproduced below for reference.



Per these reactions, SiC can react with water and oxygen to form silica, or with oxygen to form SiO or SiO₂. SiO is a gas and thus does not contribute to a passive film, and liquid water rapidly dissolves silica, which does not form a persistent film on the surface of SiC following hydrothermal corrosion [11, 14, 80]. Thus, the corrosion rate of SiC is dominated by Eqn. 6.2-Eqn. 6.9, the reaction of oxygen or water with SiC, rather than diffusion through any film of corrosion products. The observed kinetics and microscopy from this work is in agreement with this understanding; all samples initially lost mass linearly, and in the presence of oxygen, eventually transitioned into non-linear behavior. For the purposes of the kinetic evaluation, the polished SiC data is presumed to represent the actual corrosion rate of SiC. A discussion of the polishing effects is included at a later point.

Given that there are eight potential reactions that are expected to occur to corrode SiC, a general Arrhenius rate equation can be given by Eqn. 6.10-Eqn. 6.12,

$$\text{Rate}_{deox} = A_1 e^{-\frac{E_{a,1}}{RT}} + A_2 e^{-\frac{E_{a,2}}{RT}} + A_3 e^{-\frac{E_{a,3}}{RT}} + A_4 e^{-\frac{E_{a,4}}{RT}} \quad \text{Eqn. 6.10}$$

$$\text{Rate}_{ox} = [\text{O}_2] A_5 e^{-\frac{E_{a,5}}{RT}} + [\text{O}_2] A_6 e^{-\frac{E_{a,6}}{RT}} + [\text{O}_2]^3 A_7 e^{-\frac{E_{a,7}}{RT}} + [\text{O}_2]^2 A_8 e^{-\frac{E_{a,8}}{RT}} \quad \text{Eqn. 6.11}$$

$$Rate = Rate_{deox} + Rate_{ox} \quad \text{Eqn. 6.12}$$

where, A_i and $E_{a,i}$ are the pre-exponential factor and activation energy, respectively of reaction number “i”, R is the universal gas constant, T is the temperature in Kelvin, and $[O_2]^n$ is the concentration of oxygen in wppm raised to the reaction order “n”.

Given that the activity of water is always one, Eqn. 6.10 reduces to the number of $A_i e^{-\frac{E_{a,i}}{RT}}$ terms required to fit the deoxygenated reaction data. Beyond this, the ability to infer mechanistic data is limited. The rate equation of oxygen reactions is more easily evaluated and simplified. By initially assuming that each of the reaction equations Eqn. 6.2-Eqn. 6.5 follow elementary reaction steps, the variation of oxygen concentration in the present work can elucidate the overall reaction order. Additionally, if multiple reaction pathways significantly participate, this can be inferred by the Arrhenius plot. As a first step the reaction rate equation was treated in its simplest case: one step with a high degree of rate control dominates each condition. This is equivalent to Eqn. 6.13,

$$Rate = A_{deox} e^{-\frac{E_{a,deox}}{RT}} + [O_2]^n A_{ox} e^{-\frac{E_{a,ox}}{RT}} \quad \text{Eqn. 6.13}$$

Where the activation energies and pre-exponential factors are now simply the overall reaction rate and not assigned to a specific reaction.

Further insight may be gained by utilizing transition state theory (TST) to assign scientific meaning to the pre-exponential factor [152-155, 213]. TST is able to accomplish this when a single step has a high degree of rate control (and thereby the kinetics data adequately represents that single step) and does not react so quickly as to make the energy distribution no longer be described by the Boltzmann distribution [166, 167]. The first of these must be assumed true and evaluated based on the reasonableness of the resulting kinetics properties, while the second is certainly valid given the speed of the present reaction system. Incorporating TST into Eqn. 6.13, and using the SREA method detailed in section 5.6.1 [151] to convert bulk oxygen concentration to approximate surface concentration leads to Eqn. 6.14,

$$Rate = C_m \frac{Tk_B}{h} \left(e^{1 + \frac{\Delta^\ddagger S^\circ_{deox}}{R} - \frac{E_{a,deox}}{RT}} + \theta_{O_2}^n e^{1 + \frac{\Delta^\ddagger S^\circ_{ox}}{R} - \frac{E_{a,ox}}{RT}} \right) \quad \text{Eqn. 6.14}$$

Where $\Delta^\ddagger S^\circ$ is the standard entropy of activation of either the deoxygenated or oxygenated reactions, as noted, k_B and h are the Boltzmann and Planck constants, $\theta_{O_2}^n$ is the presumed fractional surface coverage based on the bulk oxygen concentrations, and $C_m = 7.0 \times 10^{-5}$ and is a conversion factor from units reacting mol fraction of SiC/s to $\text{mg}/\text{cm}^2\text{s}$. It can be shown that $\theta_{O_2} = (1.03 \times 10^{-6} - 1.03 \times 10^{-9} T)[O_2]$ for SiC in this range.

In deoxygenated conditions, the oxygen-relevant term goes to zero and the kinetic parameters are determined by Eqn. 6.15, which can be evaluated similarly to the more conventional Arrhenius plot as the left side of the equation versus $1000/T$.

$$\ln\left(\frac{\text{Rate}}{T}\right) = \ln\left(\frac{C_m k_B}{h}\right) + 1 + \frac{\Delta^\ddagger S^\circ_{deox}}{R} - \frac{E_{a,deox}}{RT} \quad \text{Eqn. 6.15}$$

Similarly, in the oxygenated conditions,

$$\ln\left(\frac{\text{Rate} - \text{Rate}_{deox}}{T\theta_{O_2}^n}\right) = \ln\left(\frac{C_m k_B}{h}\right) + 1 + \frac{\Delta^\ddagger S^\circ_{ox}}{R} - \frac{E_{a,ox}}{RT} \quad \text{Eqn. 6.16}$$

where the Rate in each condition is obtained using the linear portion of the plot (i.e, up to the time where significant nonlinearities occur). For example, the first 400 hours at 1ppm O₂ and 350°C were used for the rate analysis, but the 400-600h data was excluded due to non-linearity. For the conditions in this study, Eqn. 6.15 and Eqn. 6.16 were used to generate Figure 6.1 where the lines in that figure represent the empirical best fit line to the present data, with resulting kinetic parameters given on each figure. The listed error corresponds to the expected variation from the data scatter for the linear best fit process. For Figure 6.1b, a reaction order of 1 was assumed. This is further discussed in section 6.3.3.

Compiling these data together, the final reaction rate can be found by Eqn. 6.17, where (1+SA) is the fraction of true-to-projected surface area, relevant for rough samples.

$$\text{Rate} = \frac{0.1458}{1 + \text{SA}} T \left(1.09(1 - 10^{-3}T)[O_2]e^{-\frac{1.275 \times 10^4}{T}} + 7.91 \times 10^{-6}e^{-\frac{7.39 \times 10^3}{T}} \right) \quad \text{Eqn. 6.17}$$

6.3.2 Discussion of the Potential Reaction Mechanisms in the Absence of Oxygen
As expected from Figure 4.17 the error bars in the Figure 6.1a) are quite large, with correspondingly uncertain activation parameters. Thus, while the initial assumption that water reacts with SiC via a single pathway is empirically workable, its accuracy cannot be evaluated in the present study due to the size of the error. It is possible, for example the “true” kinetics plot will be non-linear. In such a case, two or more reactions will necessarily be active and the current data must be seen as a combination of the active reaction kinetics parameters. In that case, the present results would not have a great deal of scientific meaning.

If only one reaction is dominant, then the present kinetics parameters may hold some meaning. In particular, the standard entropy of activation, which is -240 J/mol K, is far too negative to correspond to a single bond. [165]. For example, water at 300°C at 15 MPa pressure has an entropy of 180 J/mol K [110]. If the entire water molecule were to be effectively frozen over the reaction step, the entropy loss would not be equivalent to the entropy of activation found here. Thus, while the reaction is clearly associative, the entropy must correspond to at least two associative steps in the reaction mechanism, each of which with a non-negligible degree of rate control. Such a mechanism could be related, for example, to a certain orientation of water molecules on the surface followed by bond re-ordering before any actual reaction with SiC.

It may also be related to the concentration of hydroxides in the water. Hirayama et al [74] found a strong positive correlation of the corrosion rate of sintered α-SiC with the pH of the solution. In this case, for pure water, either a free hydroxide would have to migrate near the surface, adsorb,

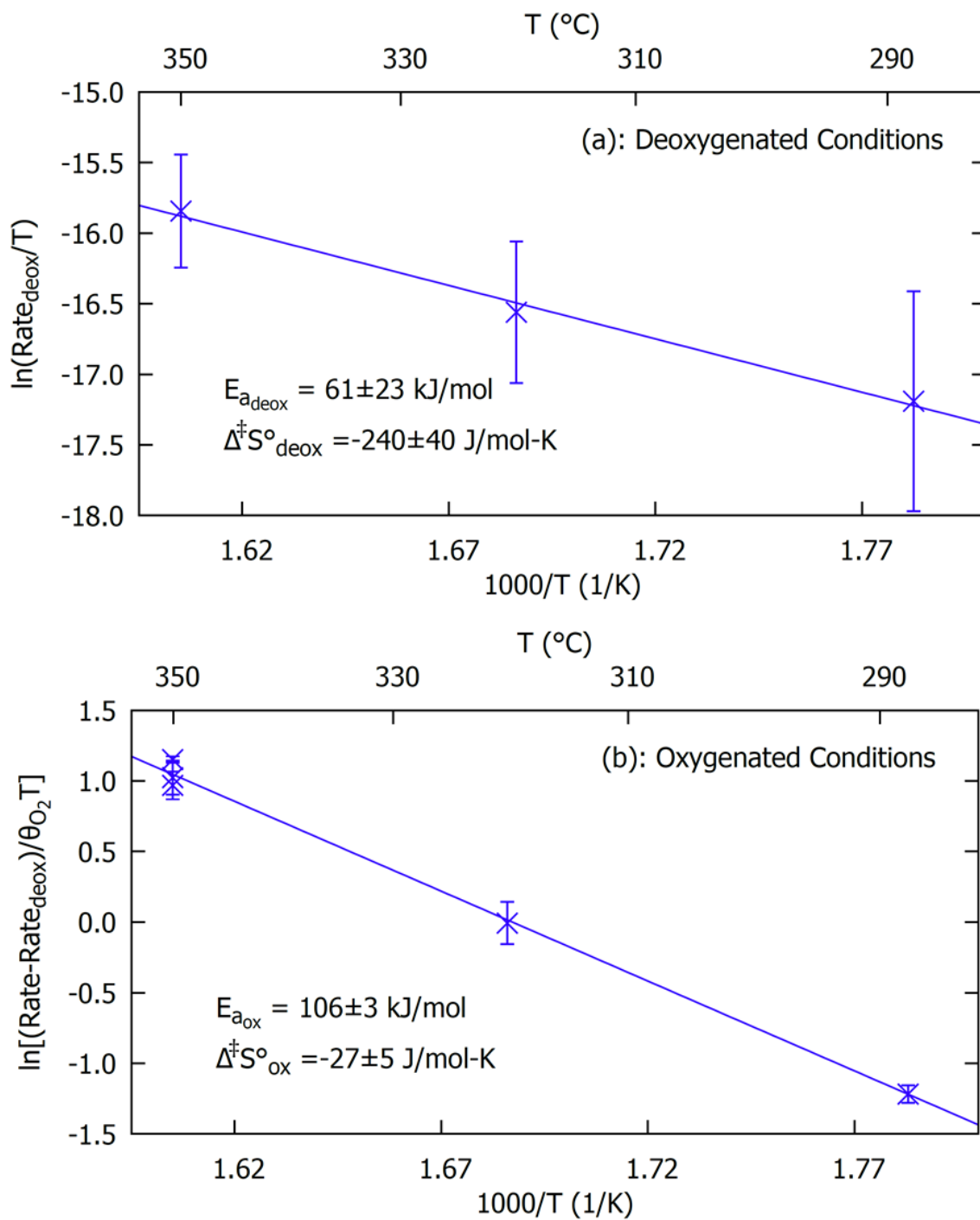


Figure 6.1: Kinetics plots of the mass change data in the uniform-attack regimes of (a) deoxygenated, and (b) oxygenated conditions using an oxygen reaction order of 1.

and react, or water on the surface would have to dissociate and subsequently react. The present data is not sufficient to evaluate these possibilities, which will likely require simulation work.

6.3.3 Discussion of the Potential Reaction Mechanisms in the Presence of Oxygen
The effects of oxygen attack on SiC are more easily interpreted than the effects of water attack given the substantially lower error in the measurement, relative to the size of the mass change. Figure 6.1b shows clearly a linear plot for the temperature dependence of the mass change kinetics of SiC under oxygenated conditions. This implies that a single step with a high degree of rate control dominates under these conditions. Unlike the deoxygenated plot, the error is low enough that it is unlikely more than one such activation pathway contributes to the corrosion in the presence of oxygen.

It should be noted here that the reaction order is also determined from this analysis, since three oxygen concentrations were used at the 350°C condition. By fixing the reaction order, n , to 1, the best fit was obtained, such that the three oxygen conditions collapse to a single point, within error, when analyzed with Eqn. 6.16. This is clear on Figure 6.1, where no distinction can be made between these points and each fits the line within error. From this, it is clear that a single oxygen molecule is involved in the activation step, but little else is determinable.

Recalling Eqn. 6.2-Eqn. 6.5, there are only two of these which involve a single oxygen molecule, one producing C and SiO₂, and the other CO and SiO. Both of these reactions are possible, and both may occur. Prior work has discovered C on the surface of SiC corroded in capsules [75], implying that Eqn. 6.4 is active. While products of Eqn. 6.2 were not observed, neither CO nor SiO are detectable in solution as they may both react to form CO₂ and Si(OH)₄ and be removed by filtration. Thus, a lack of observation does not imply inactivity in this regime.

Further, Eqn. 6.2 and Eqn. 6.4 may occur via a similar activation step. For example, if breaking of the Si-C bond is substantially rate-determining [97], a subsequent flow of electrons can lead to either both oxygens bonded with Si, yielding SiO₂ and C, or with one oxygen bonded to each, yielding SiO and CO. Under such a mechanism, the orientation of the oxygen on the surface of the SiC may be the driving force behind how the reaction proceeds, leading to similar entropies of activation in both reactions. As both would proceed primarily through the Si-C bond breaking, the activation energy would be substantially similar, as well.

Regardless of the degree of activity that Eqn. 6.2 and Eqn. 6.4 exert for SiC corrosion, at the least, Eqn. 6.4 likely occurs non-negligibly due to the observation of some surface C [75]. This implies a viable mechanism for Eqn. 6.3 and Eqn. 6.5 under these conditions. Rather than proceeding through a single step, the formation of the final CO and CO₂ products could take place following C formation via reaction Eqn. 6.4. Such reactions would not impact the overall corrosion rate of SiC, but their viability may have scientific value worth noting.

Regarding the activation parameters themselves, the activation energy with respect to oxygen is substantially greater ($\sim 1.7\times$) than the mean activation energy with respect to water. While this has the effect of significantly decreasing the exponential part of the rate constant, the pre-exponential factor of the rate constant increases, more than compensating for the decrease of the exponential. The standard entropy of activation is responsible for this, being ~ 210 J/mol K larger

in the oxygen reaction compared the water reaction. In contrast to the standard entropy of activation in the presence of water, which is too small to correspond to a single elementary step, the entropy with respect to oxygen is well within the range of reasonable values for a single step, such as those potential activation steps proposed above for Eqn. 6.2 and Eqn. 6.4. Despite the increase compared to water, the standard entropy of activation is still clearly negative implying an associative reaction. This is expected and reasonable, given that the reaction is a surface reaction, requiring the binding of a free gas. Further evaluations of the mechanistic meaning of the activation parameters is left to a future study.

6.3.4 Grain Boundary Attack and Enhanced Grain Recession

No grain boundary attack within the sample error was observable on SiC samples exposed to deoxygenated water of the sample using AFM. No enhanced recession of grains with any particular orientation was observed. Correspondingly, no such attack is observable under SEM examination of the cross-sections. This does not require that grain boundaries are not susceptible to corrosion under these conditions. Per Figure 4.17, the amount of mass change observed corresponds to a thickness recession of only 30-60 nm across all three conditions. Therefore, the enhanced recession may only be observable at higher exposure times.

In oxygenated environments, however, grain boundary attack was significant. As shown clearly in Figure 4.20 and Figure 4.21 the surface is substantially etched. Moreover, in cross-section, it is clear that the preferential grain boundary attack proceeds to about 4 μm below the surface. This is evident in Figure 4.21a and b, where grain boundary attack is present, but not accompanied by large amounts of grain fallout. At longer times, the effect is more dramatic, with greater depth of attack and fallout more extensive, consistent with observed surface microscopy and mass change data. In the presence of oxygen, therefore, SiC will eventually undergo significant increases in the observed mass loss, corresponding to grain fallout and the kinetic relationships of section 6.3.1 will underestimate the mass change. This effect is most developed in the exposure at 350°C and 4ppm O_2 where the mass change rate is $\sim 3\times$ larger than in the linear case. However, there is no indication that the rate has peaked in a steady state grain fallout regime and additional testing would be required to determine what this steady state rate is. It is likely that the steady state grain fallout rate and the transient to reach that rate once grain fallout onsets will be dependent on the grain size and thus such a study would require samples with a variety of microstructures. This is well beyond the scope of the present work.

6.3.5 Polishing Effects

Polishing does not have any statistically meaningful impact on the corrosion rate in the absence of oxygen, especially when correcting for true versus observed surface area. In oxygenated water, however, unpolished samples clearly corrode substantially faster than the polished samples. Moreover, even when the surface area is corrected by the expected 35% larger true area in unpolished samples, the polished and unpolished mass change curves do not align. This is particularly obvious in Figure 4.19a, corresponding to the NWC exposure. As previously discussed, the polished curve is statistically linear and the unpolished curve is as well.

In the more aggressive 350°C exposures where grain fallout effects are most clearly observed, both the unpolished and polished sample data also becomes non-linear. However, the incubation

time to non-linearity is longer for unpolished than for polished samples. Consider especially Figure 4.19b (the 1ppmO₂ exposure). While the polished sample visually enter the non-linear rate regime following 400h, it is less clear for the unpolished samples, and use of a best-fit line is required to show it. At 4ppm O₂, the non-linearity is much more clear following 400h, but again is only clear following 200h when a best-fit line for the first 200h is extrapolated to 400h. In contrast, the polished data shows clear nonlinearities visually.

This is most reasonably explained by consideration of the implications of enhanced roughness on grain fallout. In an unpolished sample, there are many peaks and valleys in the surface (see Figure 4.14a, for example). It is quite likely that many of these contain grain boundaries, which by virtue of their location, would be shorter, perhaps much shorter, than the average grain boundaries on a flat surface. When grain boundaries are sensitive to attack, these shorter boundaries will be fully removed (leading to grain fallout) prior to substantial removal of the grains presenting from the flat portion of the sample. If this mechanism is governing, it would be expected that the grain fallout regime would very quickly onset in the unpolished samples. As grain fallout of the flat regions begin, eventually these shorter boundaries would be reduced in number density through elimination, and the corrosion rate should begin to converge to that of the flat samples, when surface-area corrected. This is consistent with the data previously described and is most clearly shown for the exposure to 4ppm O₂ at 350°C, where the rate of unpolished and polished samples is statistically the same between 200 and 400h and also between 400 and 600h.

6.3.6 Comparison of Current and Previously Reported Results

To understand how this study's results compare to literature, Figure 6.2 is presented below. In this figure, the various exposure conditions from each study were input to Eqn. 6.17 to generate a predicted rate from each study, shown in filled purple circle makers on the graph. The inverted green triangles then show the results of each study's experimental findings. Several points should be noted about this figure. Importantly, this work is internally consistent. This is shown by the first data point which represents the corrosion of the out-of core samples from the next section.

Many of the other studies present data from conditions not directly modeled by Eqn. 6.17. For example, most studies are observed to use PWR water (including Li and B additions) at 360°C. This is both a little beyond the temperature range of the present work, and includes Li and B, which are not modeled in Eqn. 6.17, and may have an impact. At first glance, Li and B would not be expected to affect the corrosion very much. This is because of the agreement seen between Eqn. 6.17 and the results of the MITR exposure in this work (first datum point in the figure), which had Li and B additions. However, it is entirely possible that temperature has a significant effect on the impact of Li (more likely hydroxide) and B on the corrosion of SiC at higher temperatures, while it is negligible at lower temperatures.

Specifically, it may be that other reaction mechanisms with water are observed to be impactful at 360°C which are not active, even at the lower temperatures in this work. For example, if a reaction mechanism involving hydroxide has a higher activation energy than observed in the

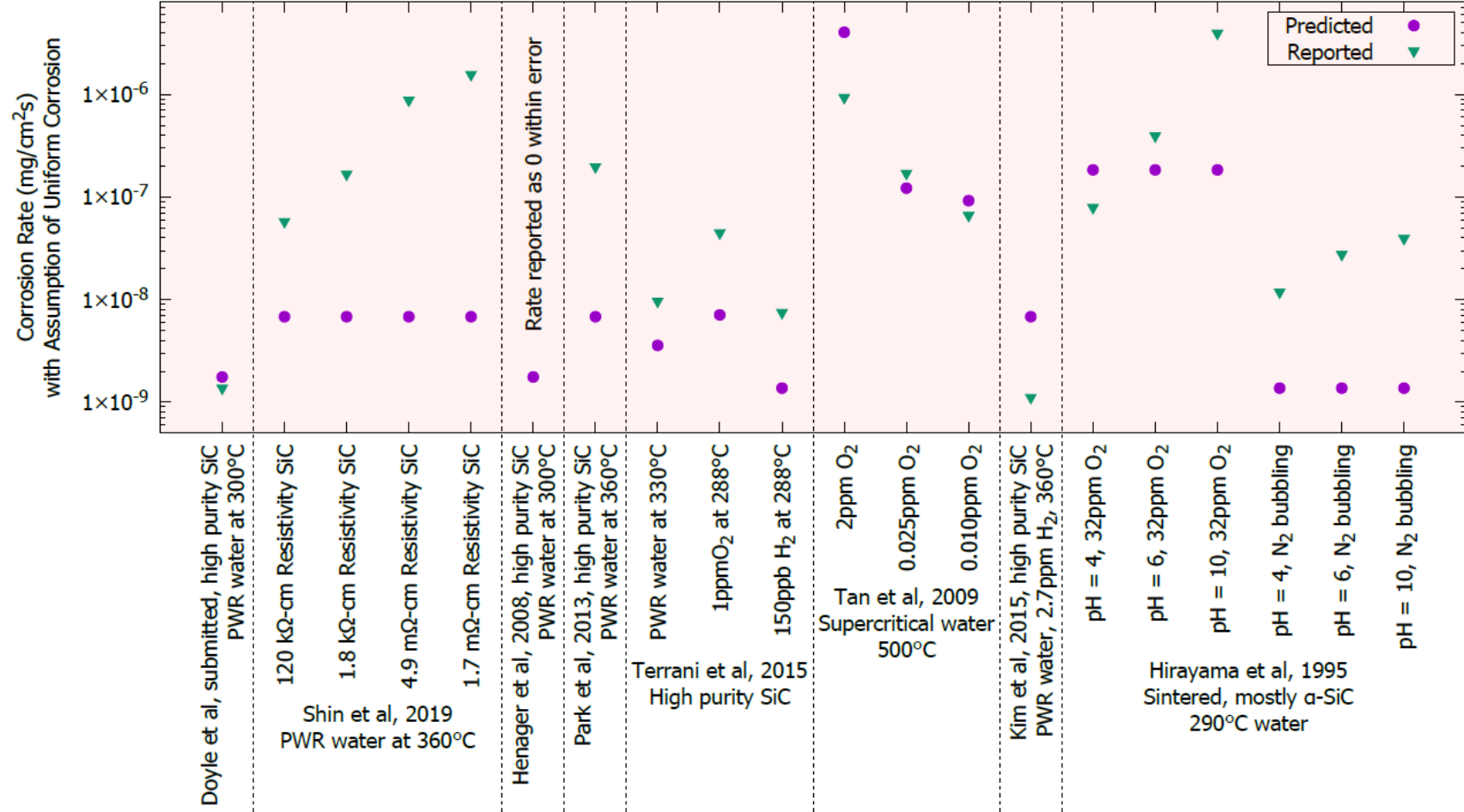


Figure 6.2: Comparison of results from published studies (inverted green triangular points) to results predicted from this study by applying Eqn. 6.17 to the test parameters of each study. References listed on x-axis are [11, 74, 80, 94-96, 100] and the following section of this work.

present work, it may, provided an appropriate rate constant, dominate at 360°C under PWR chemistry. However, in such a case the hydroxide effect would not necessarily appear in the present study's MITR results due to the lower activation energy. As a second option, studies such as Shin et al found substantial grain boundary attack, even in the most corrosion resistant samples, whereas no such attack in deoxygenated conditions was observed in this work. If hydroxide preferentially attacks incoherent grain boundaries (these have been suggested to be especially vulnerable to corrosion [97]) at high temperature, the additional material loss would be reflected in the reported corrosion rate.

An additional factor arises from differences in the surface preparation and material types in the different studies. For example, the Shin et al [100] work displays four data points corresponding to four different sample resistivities. As the present model, Eqn. 6.17, does not account for resistivity, only the high purity (high resistivity) samples are comparable to the present work. While even that point is significantly different from the predictions in this work, it is expected that the effects of Li/B additions at high temperature together with the uncertainties in this work's deoxygenated test results will largely account for the remaining discrepancy. However, additional work is needed to confirm.

Terrani et al [11] does not mention polishing condition. However, as mentioned previously, polishing does not seem to have a significant effect at low temperature in deoxygenated conditions, but the data points may be in more agreement than apparent from the graph depending on the surface condition of the sample. These data highlight the uncertainty in the present correlation for deoxygenated samples, which is admittedly quite large as previously discussed. The implication from the present comparisons is that additional exposures in the present study would yield some increase in the observed reaction rate as the errors decrease.

It is somewhat surprising that data from Tan et al [95] agree so well with the present predictions, given that they take place in supercritical water, where some passivation due to SiO₂ formation should retard the corrosion process. However, the supercritical water flowrate in that study was fairly fast, 1m/s and no protective behavior was observed. As such, the reaction modelled a simple surface reaction without diffusion and compares well to the present results. This may lend some credence the idea that at high temperatures, Li and B play an increased role in SiC dissolution.

Finally, the present data agree surprisingly well with the results of Hirayama et al [74] in the oxygenated case. Given that the materials in that case were sintered SiC, they were expected to corrode more quickly than CVD SiC, which they do, but by a rather small amount. Because the present work investigated pure water (pH ~ 5.6 at temperature) and Eqn. 6.17 does not model pH, the correlation found by Hirayama et al with respect to pH is such that the model would be expected to overpredict the low pH and underpredict the high pH condition. It is further consistent that the model underpredicts the rate in deoxygenated environments considering the deoxygenating method of bubbling Ar. The present work employed H₂ to scavenge O₂ which has been shown to be more effective in deoxygenating water than unreacting gases. This is shown here and also explicitly in [80].

6.4 MITR Exposures of Uncoated SiC

The exposure of SiC in the absence of radiation provides a baseline corrosion rate and kinetic parameters for comparison with kinetic model predictions. However, in a reactor environment both radiation damage and an increase in aggressive species due to radiolysis of water will occur. This section explores how these additions affect the corrosion of SiC.

6.4.1 Extrapolation of Mass Change with Assumption of Uniform Dissolution

The data from Figure 4.22 was extrapolated assuming uniform mass loss with linear kinetics, and the thickness recession after five years is presented in Table 6.1. For all samples except the CMC SiC sample exposed in core, the extrapolated thickness loss was well below the standard proposed for this work. The extrapolated thickness loss of the CMC exposed in-core in the MITR loop was 120 μm at 5 years, which exceeded the allowable corrosion standard proposed for SiC cladding in this work. However, it should be noted that a CMC with an initially hermetic CVD overcoat will likely corrode similarly to CVD SiC unless significant cracking or chipping of the overcoat occurs, when accounting for the additional surface roughness. Further work is needed on such samples to evaluate degradation behavior. In addition to the loss of cladding thickness, silica deposition in the colder parts of the plant are a concern that must be addressed when considering SiC-based cladding. An initial analysis of this effect has been given by Terrani et al [11] in the absence of any filtration and indicates that saturation of silica in the water does not occur (and thus deposition does not begin) until well after 2 years of operation at the dissolution rates in this work (c.f. Figure 16 of that work). The in-core CMC samples degrade fast enough to become a concern from this evaluation. Naturally, implementation of silica filtering would likely be recommended if SiC cladding is used in a plant, and plant-specific dissolution and deposition simulations should be determined, as relevant.

6.4.2 Radiolysis Product Concentrations

The increased corrosion rate observed on the in-core specimens can likely be attributed to a combination of radiation damage in the samples [91, 214, 215] and to the presence of oxidizing radiolysis products [120, 216-218]. Determining the extent of each in the core requires calculation of the differences in radiolysis concentrations in each section of the loop. This was accomplished using the previously described radiolysis model (see section 3.3.1 and Appendix C). For these calculations, the three regions (in-core, above-core, and out-of-core) were assumed to have a constant energy deposition rate across each region, as reported in Table 3.7. Results of these calculations are presented below for select radical (Figure 6.3) and stable (Figure 6.4) radiolytically-produced species. The in-core, above-core, and out-of-core regions are indicated by background shading in each figure and the position of the SiC samples are noted by dashed vertical lines. The x-axis indicates elapsed time from the water entry into the loop at the core inlet. Figure 6.3 and Figure 6.4 show the prominent radical and stable chemical species resulting from radiolysis using the basic model outlined in Table 3.7 and Table 3.8.

In the radiation regions, equilibrium is achieved within 0.1 ms, in agreement with other works [216, 217]. The oxidizing radical species are always present at low concentrations in the radiation regions and are quickly consumed as the water enters the out-of-core region. As such, they are considered to not directly impact the above-core or out-of-core corrosion rates.

Table 6.1: Predicted thickness recession (μm) after 5 years of exposure using the data in Figure 4.22 and Figure 4.23. HR refers to high purity and electrical resistivity, and CMC refers to tubes made from ceramic matrix composites. The assumed acceptable standard is 50 μm recession in 5 years.

<i>Type of SiC</i>	<i>In-Core</i>	<i>γ Radiation</i>	<i>Water Only</i>
<i>R&H HR</i>	3.5	1.7	0.5
<i>Coorstek HR</i>	4.7	1.0	0.8
<i>Coorstek HR2</i>	3.0	0.7	0.9
<i>Single Crystal</i>	0.6	0.3	0.2
<i>Present CMC</i>	120	5.4	-2.4

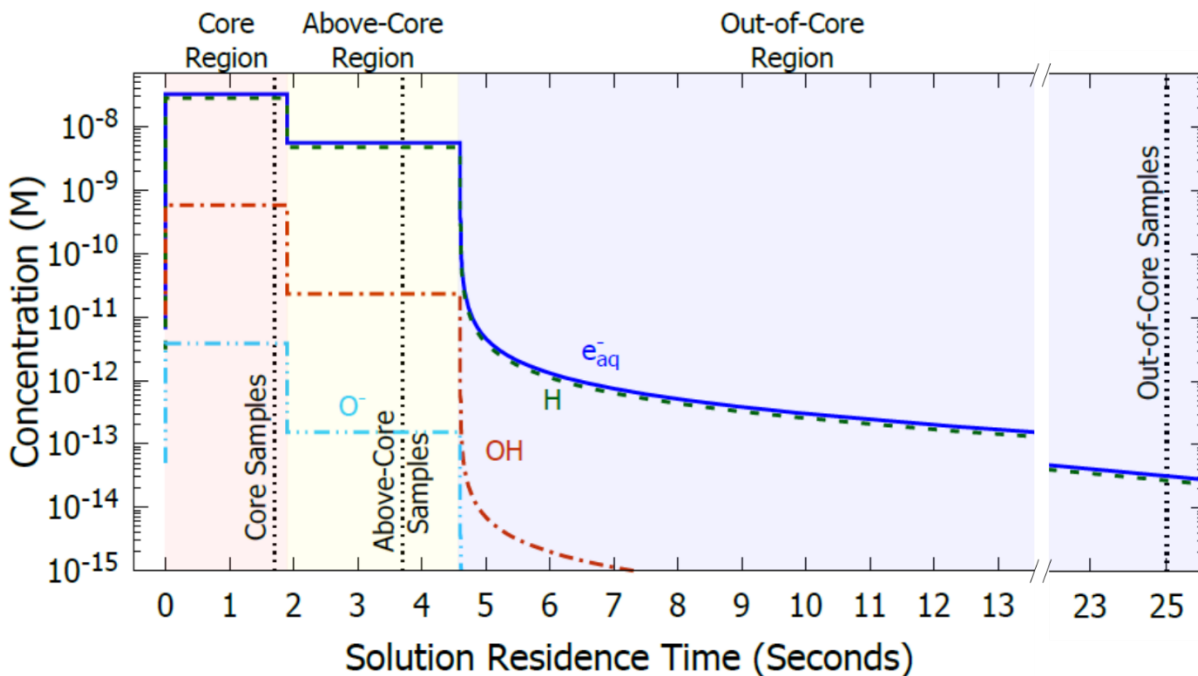


Figure 6.3: Calculated selected radical species concentrations (mol/L) for each region of the MIT loop versus the time the solution has spent in the loop since entering the core.

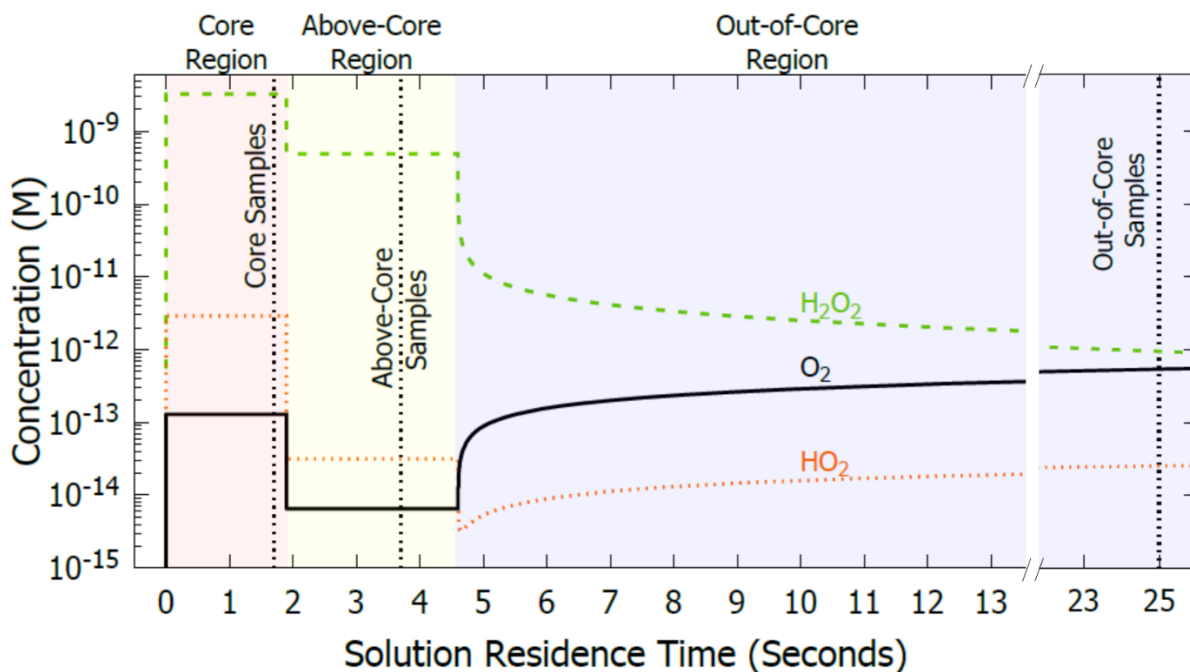


Figure 6.4: Calculated stable species concentrations (mol/L) for each region of the MIT loop versus the time the solution has spent in the loop since entering the core. The model used the parameters listed in tables Table 3.7 and Table 3.8. Corrosion-relevant Radiolysis Products and Concentrations Out-of-core.

The concentration of stable species, however, warrants more discussion. Oxygen, which is often used in autoclave experiments examining SiC, is negligible in and above the core. Out-of the core, the lack of radicals prevents significant reactions with other aggressive species (reactions 8, 12, especially), allowing its production to briefly continue, chiefly by decomposition of peroxide (reaction 21). Despite the increase in oxygen concentration, the as-calculated out-of-core concentrations are still several orders of magnitude lower than typical testing conditions with oxygen, and are not expected to contribute to corrosion, as prior and forthcoming work demonstrates [11, 130, 219]. Moreover, the present radiolysis model ignores the scavenging reaction of O_2 with H_2 to form water which is catalyzed by metal surfaces. This reaction is likely very active in any realistic system, and would further reduce the concentration of oxygen [220]. HO_2 similarly is considered inconsequential.

Of the remaining stable species, H_2O_2 , as typically observed [216, 217], is the only oxidizing species which may significantly contribute to corrosion due to its initially calculated concentration. This initial concentration appears to be high enough to affect the corrosivity of the environment (relative to the core and above-core regions, especially), and coupled with its aggressiveness, it is the primary concern among radiolytically-produced species [221-223]. However, in the AECL report used in this work, it was noted that the decomposition rate constant of hydrogen peroxide (which governs the stable species' concentrations out-of-core) is variable depending on the containing system (including the extent of oxide film formation on the metal tube walls) [120]. This effect is evaluated in Figure 6.5 (solid lines), where the concentrations of stable species at the out-of-core sample location are plotted against the decomposition reaction rate constant of peroxide. While in and above the core the peroxide and HO_2 concentrations were insignificantly affected by these rate constant changes (and oxygen concentrations remained negligible, below 10^{-12} M), increasing wall contact (i.e., catalyzing the reaction) drastically reduces the peroxide concentration in the out-of-core region, with only minimal increases in the O_2 and HO_2 concentrations. Assuming a fully turbulent flow (the flowrate and geometry suggest a Re number of at least 5×10^7 and a viscous sublayer thickness on the order 10 μm), the assumption of increased catalysis is reasonable. Thus, the corrosion rates outside of the core should be reflective of corrosion in the absence of radiolysis products.

This conclusion is further reinforced by consideration of uncertainties in the mechanism of the AECL model, which notes that the decomposition mechanism can proceed in one of two ways: 1) straight to oxygen and water (the reaction used to generate the results above), or 2) through an initial decomposition to OH radicals which may eventually produce oxygen in subsequent reactions. Both mechanisms are modelled in Figure 6.5, with the dashed lines indicating a decomposition to OH radicals and solid lines indicating the immediate production of oxygen. In the latter case, all stable species reduced to negligible concentrations (radicals remain below 5×10^{-12} M, especially under the high-contact conditions. This is caused by the many paths that OH radicals can take (reactions 3, 5, 6, 15-17, 29, 31, 40, 42), only two of which result in oxygen production (reactions 16 and 17). Many of the other reactions produce more stable species, such as OH^- and H_2O , thereby suppressing the formation of HO_2 and O_2 , as modelled in Figure 6.5.

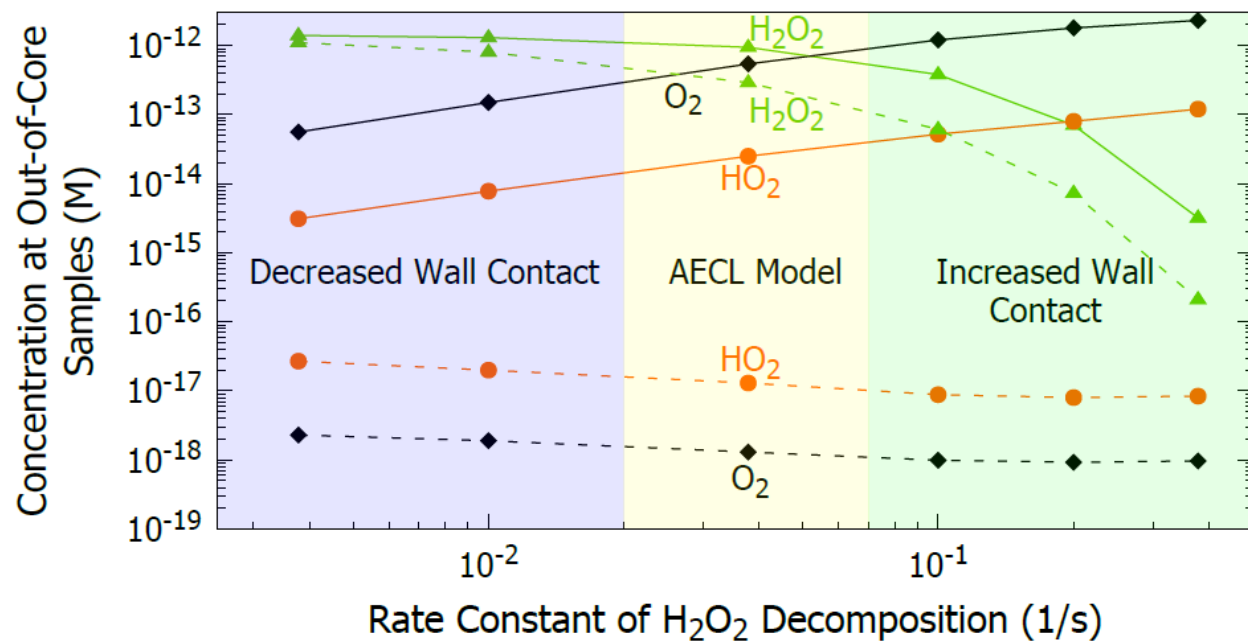


Figure 6.5: Effect of the dissociation rate constant of peroxide on the concentration of stable species at the out-of-core location. The concentration of H_2 is stable at the input of 1.48 mM H_2 and is not shown. Solid lines indicate the decomposition occurs by the mechanism set forth in the model (production of water and oxygen). Dashed lines note the concentrations of direct decomposition to OH radicals.

None of the changes modelled in Figure 6.5 for the out-of-core locations translate to significant peroxide concentration changes in the core and above-core regions. Thus, radiolysis products in these regions can be approximated by the concentrations given in Figure 6.4, with radiolysis effects considered negligible out of the core.

6.4.3 Corrosion in the Absence of Radiation

In the absence of radiolysis products, and in water with a low pO_2 , corrosion proceeds by reaction with water only. As shown in Figure 4.22 and Figure 4.23 the error in the individual sample masses is a substantial fraction of the overall mass change. This results in no statistically significant difference in the mass change of any of the monolithic samples. Previous LWR results agree [130] that there is no statistical difference for the different forms of SiC in hydrogenated environments in the absence of irradiation at 288°C, and this finding is reinforced by the lack of any observation of local attack in Figure 4.24.

It is important to note that this result may not translate to other deoxygenated water conditions and will not translate to oxygenated conditions [130]. Shin et al [100] and Kim et al [80] have reported significant effects of SiC resistivity and dissolved hydrogen, respectively, on the corrosion rate in deoxygenated environments. However, their tests were conducted at 360°C rather than the 300°C used in this work. Corrosion studies evaluating sintered SiC (which is known to be substantially more susceptible to corrosion than pure SiC [15, 25]) have observed significant increases in the corrosion rate as a function of pH [25, 74]. While Kim et al [25] imply that, unlike sintered materials, CVD SiC is not greatly impacted by pH changes (if at all), the response of CVD SiC in controlled-pH environments has not been examined. Such studies would help to evaluate the extent to which the enhanced corrosion of LR SiC observed by Shin et al. [100] is caused by higher temperatures or pH.

The CMC SiC does not behave similarly to the monolithic samples. Despite post-exposure heat-dehydration to drive off any water trapped in pores/cracks of the CMCs before weighing, a net increase in mass over the course of the exposure was measured for the out-of-core sample. One possible explanation is the formation of internal silica in the CMC samples due to water ingress through the fibers exposed on the ends or at cracks in the outer monolith. The dominant corrosion reactions in this chemical system involves silica formation and subsequent dissolution [11, 74, 130, 204, 219]. This mechanism assumes that SiO_2 dissolves completely after forming. In the event that water is able to enter the matrix through pores, cracks, or exposed interfaces, the amount of water present in the sample will be small compared to the surface area of SiC, and a buildup of SiO_2 without dissolution into solution is possible. These results are in contrast to the conclusions from Stempien et al [205], which showed for longer tests (177-340 days) in the same conditions, that all CMC samples lost mass overall. This discrepancy may be explained by the shorter testing time for this work. It is possible that the present results reflect a temporary mass gain, which is negated over time. For example, this could happen if water channels into the CMC begin to expand, allowing enough water in to begin dissolving away additional SiC. However, it should be noted that all CMCs are not constructed the same way, and fully sealed CMC may behave differently. Additional testing is required to determine these effects.

6.4.4 Effect of Radiation Damage and Radiolysis on the Corrosion Rate

The effects of radiation damage and radiolysis are more nuanced and material-specific than the water-only tests. Several points are noteworthy from this data, and a quantitative discussion is available in the Appendix D. First, it should be observed that the mass change of the polycrystalline samples are statistically equivalent in the above core (radiolysis) regime. This is also observed with the out-of-core samples which appeared to be chemically stable. As the only difference between the out-of-core and above-core sections is the presence of peroxide with concentrations on the order of 10^{-9} M, this result indicates that peroxide may not enhance the corrosion of HR SiC as much as oxygen enhances it (if at all). This is an important result given that oxygen is a negligible oxidant under the present reactor conditions, while peroxide is significant.

Second, in both radiolysis and radiation damage conditions, single crystal SiC appears to degrade more slowly than polycrystalline SiC. Differences between these samples may come from two sources: 1) roughness and 2) attack of grain boundaries or grain fallout. As clearly demonstrated in Figure 4.24 localized attack is not noticeable on the out-of-core or above-core samples, and no visual differences are clear between those samples regardless of type, implying no substantial local attack from radiolysis products. It is clear from that figure, however, that the CVD samples are quite rough, and this is taken to be the primary reason for the difference between the single crystal and polycrystalline sample corrosion rates. Future tests should include polished CVD samples to better evaluate the differences between these samples and quantify grain boundary effects.

Third, the in-core polycrystalline samples corrode slightly differently. Of the six high resistivity samples, three corroded similarly, with Coorstek HR 1 appearing to possibly be anomalous (from chipping or the like), while both Coorstek HR2 samples lost mass statistically less quickly than any of the other high resistivity samples. This result was not expected and may be related to slight differences in impurities, stacking fault densities, and the like, given that all six polycrystalline samples are nominally identical in composition.

Finally, the CMC materials lost significant mass in both the radiolysis and radiation damage regimes. This implies that the initial mass gain observed in the out-of-core samples, is erased either by sufficient mass loss to overshadow remaining internal chemical precipitations or oxides, dissolution of internal precipitates or oxides, or by increase of the effective area through increased water access to the CMC interior. These possibilities raise concerns about the extent of protection from the outer SiC monolithic coating. It should also be noted that the CMC apparent surface area from dimensional analysis will be significantly smaller than the true area due to the fibrous preform having a woven texture. However, examination of Figure 4.23 reveals that the ratio of the CMC mass change per apparent surface area to that of the CVD samples is much larger in-core than above-core. This implies that the CMC did corrode faster (since the true surface area will be comparable for all samples), or significant water access to the CMC interior increased the surface area.

Thus, while this work does show that SiC corrodes slowly enough to potentially be used in service, the CMC data demonstrates that additional considerations are required. The combination

of matrix, fibers, and interphases exposed to the coolant through an as-cut end yields corrosion rates well in excess of the monolithic material. This study does not isolate the cause of the enhanced degradation, but does show the importance of protecting the interior of the CMC with a hermetic overcoat. Because CMCs differ in construction, more comprehensive testing on the specific degradation mechanisms of each CMC component (fibers, matrix, and interphases) is required to better evaluate overall CMC performance in a reactor environment.

It must be stressed that these observations are based on the limited sample set included in this work and further study with more samples is needed before they can be confirmed.

6.4.5 Comparison to Other Data Sets

The preceding sections discuss the meaning of the current results from the MITR experiment. Figure 6.6 shows the present results along with a variety of results from other sources. Reported data has been converted to uniform mass loss based on reported conditions, in order to better compare the studies. The figure is divided into three graphs, each showing a different mass change rate-range for clarity, with (a) showing the full range, (b) showing a partial zoom, and (c) showing the smallest absolute mass changes. Each graph is divided into four sections corresponding to different exposure or sample conditions. “Water Only” corresponds to unirradiated samples exposed to solution indicated on the x-axis. The “Radiolysis” block represents the present study’s above-core samples. “Pre-damage” represents studies where SiC has been irradiated prior to exposure in the solutions indicated. Finally, “In-core” represents samples exposed to neutron irradiation and coolant simultaneously. More full descriptions of each condition are provided in Table 6.2.

A few points are worthy of consideration. First, studies on irradiated SiC are highly varied in conditions, type of irradiation, and grade of SiC. The Park et al. study [224] involved in-situ irradiation of a large variety of CMC SiC samples with and without endcaps and monitored the corrosion rate via Si concentration. As CMC SiC varies greatly in corrosion rate based on manufacture type [205], and corrodes faster than CVD SiC when the CMC interior is exposed, as shown in this work, the orders-of-magnitude larger mass loss in that study compared to the present work is understandable. Similarly, the BWR-NWC tests corroded SiC faster than deoxygenated conditions due to the presence of 1-2 wppm O₂. Large corrosion rates are also noted for the Kondo study. In that work, CVD SiC samples were pre-irradiated with 5.1 MeV Si ions and subsequently exposed to 320°C liquid water with 8 wppm oxygen.

The main conclusion from this figure is that high quality and relevant data on as-irradiated and in-situ irradiated SiC is lacking and no constitutive relationships currently exist to connect the diverse exposure conditions given. Nevertheless, a few observations are worthwhile. First, the present work shows lower corrosion rates than other studies. However, this is not of immediate concern given the differences in the sample types and exposure conditions given in this work compared to those studies, as discussed above. Thus, direct comparison of these data is not very meaningful. However, it can be stated that the Terrani et al data [11] would be expected to be in better agreement with the present work, and no explanation is offered, aside from sample mishandling in this or that test, which could account for the discrepancy. Oxygen has a significant impact on the corrosion of SiC and if not scavenged may lead to excessive corrosion

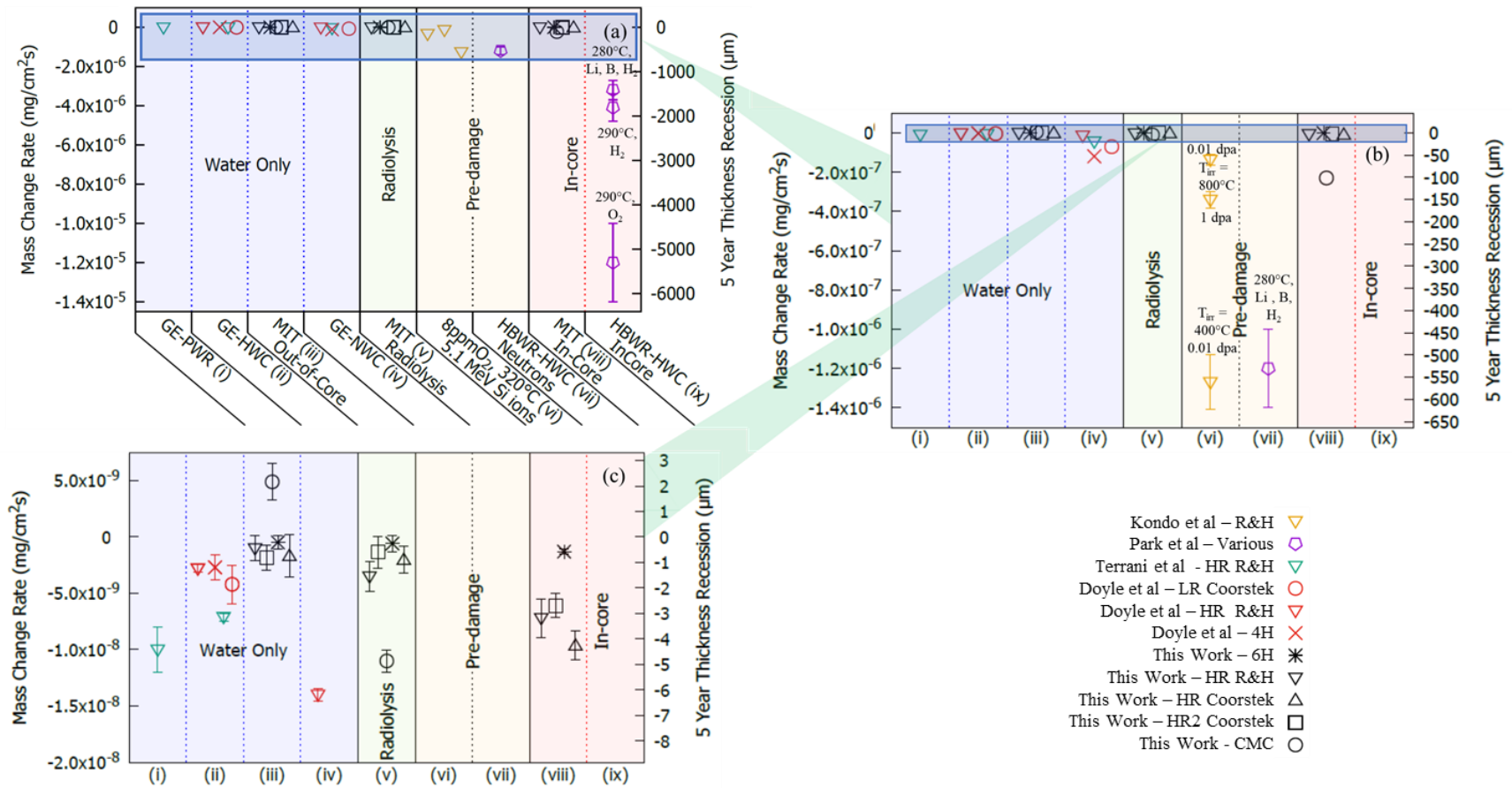


Table 6.2: Exposure conditions and samples for studies given in Figure 6.6.

Reference	Exposure Details		Sample Types
This work	MIT 1240 ppm BH ₃ , 4.3 ppm Li, pH = 6.6 300°C with 4wppm H ₂ In three conditions: In-core Shielded from neutrons, Out-of-core		6H (single crystal)
			High purity (HR) SiC from R&H
			High purity (HR) SiC from Coorstek
			CMC SiC from General Atomics
Terrani et al [11]	GE-PWR 330°C, 3.6 wppm H ₂	HR SiC from R&H	
	GE-HWC 290°C, 0.3 wppm H ₂		
	GE-NWC 290°C, 1.0 wppm O ₂		
Doyle et al [130]	GE-NWC		HR SiC from R&H
			HR SiC from Coorstek
			LR SiC from Coorstek
			CMC SiC from General Atomics
	GE-HWC		HR SiC from R&H
			HR SiC from Coorstek
			LR SiC from Coorstek
			CMC SiC from General Atomics
Park et al [224]	Halden BWR – with neutron irradiation	280-300°C 0.2-0.3ppm O ₂	Various CMC SiC materials with and without tube end-caps and with multiple joining techniques
		280-300°C 1.8-2.2 ppm H ₂	
		270-290°C 2.2-3.2 ppm H ₂ 4.5 ppm Li 1000 ppm B	
	Halden BWR- after removal of neutron irradiation	270-290°C 2.2-3.2 ppm H ₂ 4.5 ppm Li 1000 ppm B	
Kondo et al [215]	Exposed for 168 hours to 320°C water containing 8 wppm O ₂	Pre-irradiated with 5.1 MeV Si ion beam to 0.01 dpa at 800°C	HR SiC from R&H
		Pre-irradiated with 5.1 MeV Si ion beam to 1 dpa at 800°C	
		Pre-irradiated with 5.1 MeV Si ion beam to 0.01 dpa at 400°C	

of SiC. At 300°C, the present data shows that hydrogen effectively reduces the corrosion rate to potentially acceptable values even in-core, provided that CMCs can be hermetically sealed with a CVD overcoat layer. Second, the effect of defects in the CMC overcoat have not been explicitly investigated. In light of recent work indicating substantial stress buildup in SiC tubing in-core, such studies will provide clarity on the viability of SiC/SiC with a CVD overcoat. Finally, Figure 6.6 shows a clear impact of initial radiation damage on the corrosion rate of SiC. Higher temperature (320-330°C) in-core studies should thus be conducted to ensure that SiC corrosion does not increase too significantly relative to the present study.

6.5 Exposure of Coatings in the Absence of Irradiation at ORNL

6.5.1 TiN

Several points are worth noting with regard to the reaction kinetics of the TiN coatings. As with the other coatings, these are relatively impure materials with substantial quantities of C and O, as shown in Table 3.4. This may affect the coating stability and corrosion rate. The Pourbaix diagram shows that in oxygenated environments, the thermodynamically stable product is TiO_2 and in the absence of spallation, a passivating system is expected.

Moreover, the number of potential reactions is quite large (see Eqn. 4.2), making any potential mechanistic inferences difficult in the best of conditions. Of course, not all of these equations are equally likely to occur via elementary steps. For example, 2 reactions with oxygen involve 2 molecules of TiN and 2-4 molecules of O_2 . These are unlikely to proceed through a single step or even two steps given the low concentration of oxygen. Naturally, the reaction may be slow and proceed through a single rate limiting step with only two or three molecules present for each reaction, as inferred in section 6.3 for the SiC reactions. Regardless, since there is no fundamental distinction in the various reactions (i.e., TiO_2 is the only observable reaction product, since the others will dissipate from the reacting surface as gases or solutes in the solution), and the differences on the reactant side between the various reactions do not provide a method to distinguish between reactions, no mechanistic evaluation was initially expected to be valuable.

The thermodynamic expectations are confirmed by the data provided in section 4.4. TiO_2 is the only Ti-containing species observed on the surface. The phase of TiO_2 which is most stable on the TiN surface depends on the exposure condition, with anatase being most stable in deoxygenated conditions, and rutile being the most stable in oxygen. Previous work has reported similar effects, with anatase growing into rutile under solar beam heat treatment [139]. This effect has been linked to the size of the grains, where grains below 16 nm were most stable as anatase and transitioned to rutile for grains above 30 nm [225]. It can thus be inferred that the oxide film on the TiN is quite small, on the order of tens of nm. Under oxygenated conditions where rutile is the stable phase, the intensity of the spectrum is significantly larger implying much thicker oxides. The HWC data presents something of an outlier with the strongest peaks coming from what has been identified as a (Ni or Fe) TiO_3 . As these peaks are unique to the HWC case, at the higher temperatures, this oxide may not form quickly enough compared to TiO_2 .

Using FactSage7.2 again and recalculating the Pourbaix diagrams to include Ni and Fe, both NiTiO_3 and FeTiO_3 are shown to be stable in the deoxygenated conditions (except for the FeTiO_3 , which is destabilized at 350°C). It should be noted this is cursory evaluation. The actual stability lines are very close to the estimate of the present conditions and very sensitive to the N-containing product used to calculate the diagrams and also to the concentration of metals in the solution, which is assumed to 10^{-6} M, per the convention. It may be that in the given cases, the actual concentrations are significantly different than this, which would change the result. Since the impurities in this work were not directly monitored, more cannot be said as to stability of $(\text{Ni,Fe})\text{TiO}_3$ in this work. Ultimately, as this is only observed in the HWC case, where oxidation is not substantial in TiN a settlement of this question is not pertinent to the major conclusions of this work.

These observations are in agreement with the SEM cross-sectional examinations. In deoxygenated conditions, the oxide films were not observable indicating the films are likely well below 100nm. This oxide thickness is in agreement with the lack of significant increase in mass under any conditions. In contrast, oxygen reactions consumed at least hundreds of nm of the coating, or the entire coating, depending on the condition.

SEM evaluations further explain the mass losses observed in each exposure. Surface microscopy shows a generally adherent coating, with localized spallation regions uniformly spread across the sample (this is also observed at lower magnification using the relevant images in Appendix A). While this study was not able to confidently identify the ultimate causes of spallation, three possibilities are suggested which may operate simultaneously or by themselves.

First, these particular coatings had large particle defects that could extend, in some cases, through the entire film. Around these, the coating was not perfectly dense and appeared to form oxides. If such particles fall out either due to sample handling or as a consequence of the heating and cooling process growing the cracks between the defect particle and the surrounding coating, the distance to the interface may be substantially reduced, or even go to 0, exposing the interface. This is likely the method governing mass loss in the deoxygenated environments, where the coatings never fully delaminated.

Second, following either direct interfacial exposure through a scratch or defect particle removal, or indirect exposure through full oxidation of the coating (and ultimately oxidation of the interface). Under the direct exposure mechanism, both the TiN and SiC would be oxidized and exposed to coolant, leading to a $\text{TiN}/\text{TiO}_2/\text{SiO}_2/\text{SiC}$ interface. However, because SiO_2 dissolves quickly in water as shown in section 4.1.1, the coating could be chemically peeled from the interface at the rate of SiC oxidation. Under either indirect or direct exposure conditions, the stresses arising from the formation of SiO_2 and TiO_2 sandwiched between SiC and TiN could be substantial and lead to spallation.

Third, coating defects caused at deposition either by imperfect deposition parameters or surface defects (such as a pre-cracked SiC substrate region, or engraving marks) may lead to spallation by thermal cycling. The localized stresses across such defects and near edges would be different than in the bulk, potentially putting the coating into a tensile state and allowing it crack. It would

then be possible to have the above two mechanisms operating together with simple delamination to remove the coating.

It is possible that all of these contribute to coating failure (certainly for delamination by SiO_2 dissolution, the first two would have to be occurring). At least the first option, and potentially the third is quite likely to occur given the observations of local spallation and apparent removal of some macroparticles. Under deoxygenated conditions, the second option will not occur without sample damage (or instability of particular particles as a result of the deposition process) since the first since the coating does not oxidize quickly.

In summary, this first-generation TiN coating was not protective under any condition. TiO_2 was formed on the surface, as expected from thermodynamics. Under deoxygenated conditions, the oxide thickness was small enough that TiO_2 formed the anatase phase preferentially, which destabilizes when grain sizes are greater than ~ 16 nm. Thus, even though this TiN sample was not perfectly pure or stoichiometric, it was chemically stable. This does not translate to the oxygenated condition where the coating was completely oxidized and removed from the coating over the duration of the exposures. It is suggested that the primary mode of failure in this study is due to the intrinsic coating defects combined with interfacial attack. Therefore, some improvement may be gained by reduction of coating defects, but the extensive peroxide concentrations in the reactor core may lead to excessive oxidation rates that are intrinsic to the material, as discussed in section 4.5.2. Specific radiolysis experiments are needed to more properly understand the effects of peroxide on TiN corrosion.

6.5.2 Cr and CrN

The following discussion will not include the multilayer, Cr/CrN coating, which failed quickly. This failure could have been caused by poor adhesion or by thermal stresses, or both. This has not been investigated in the present work. All references to “CrN” in this section therefore only refers to the monolithic CrN.

The Cr and CrN materials behaved in a chemically similar fashion and are thus discussed together in this section. As shown by the Pourbaix diagrams in section 4.4.1, in the absence of oxygen, it is quite simply expected that only stable chromia will form, providing immunity.

In the presence of significant oxygen, the case becomes more complex. Neither Cr nor CrN are expected to form a stable Cr_2O_3 film. However, this does not on its own require that a Cr_2O_3 is unprotective. Rather, it implies the need to evaluate whether the kinetics or thermodynamics are governing. Were chromia stable, this question would not be needed as the eventuality of the process whether rapid or slow would be to form a passive film on the surface.

Given chromia is thermodynamically instable under the present oxygenated conditions, the discussion must be whether the formation of chromia is substantially faster than its dissolution. If the rates are nearly equivalent or the dissolution rate is faster than the formation rate, then the coatings will not be protected by passivation so no meaningful oxide thickness (and thus diffusion barrier to oxygen) will be developed. The coating may still be protected kinetically if the limiting reaction proceeds slowly enough as to not remove the coating over the engineering

lifespan. Finally, if the formation rate is rapid compared to dissolution, a form of passivation will develop, with the degree of protection determined by the specific difference in the reaction rates.

Prior to discussing the kinetics it must be observed that the Raman data reveal an interesting and originally unexpected result: the formation of CrO_2 on the coating surfaces. By removing Cr_2O_3 and the HCrO_4^- from consideration in the Pourbaix diagram, it is revealed that CrO_2 is a secondary oxide species. Previous work growing oxides on Cr with laser heating has shown that CrO_2 may actually form as an intermediate to the formation of Cr_2O_3 [140]. However, in the present case, as neither Cr_2O_3 or CrO_2 are stable, the CrO_2 will be able to react either to form Cr_2O_3 or the aqueous HCrO_4^- .

Additionally, the spinel is also revealed to be a stable species when considered in the Pourbaix diagram. There may be two causes of the spinel peaks in these coatings, each arising from the presence of impurity metals in the autoclave. Although the water was kept quite pure, some metal species, such as ions of Ni and Fe, will dissolve into the water from the autoclave and associated tubing to create these spinels.

One cause of the spinels is the incorporation of the impurity Ni or Fe ions into the oxide during its formation. The other is the precipitation of oxides from the coolant, without regard to the oxidation rate of the coatings. Both of these are possible, although the former is more likely considering the Raman data of the TiN. If precipitation alone were relevant, one would expect that it would also occur on the TiN coating. Instead, the only spinel-like structure appearing on the TiN is $(\text{Fe,Ni})\text{TiO}_3$, which only formed in the HWC condition. This is supported further by the structural similarity of Cr, CrN, and TiN, which share the same space group and by the fact that CrN and TiN have quite similar lattice parameters (see Inorganic Crystal Structure Database (ICSD) entries 64711 (Cr), 644769 (TiN), and 192945 (CrN)). No such spinel peaks are observed in TiN, however, even in the deoxygenated case, where the anatase peaks are not likely large enough to drown out the dominant spinel signal. Therefore, it is most likely that these spinels originate from incorporation of some Ni or Fe into the oxide during its formation.

As the oxides under deoxygenated conditions are too thin to observe in SEM, it is not possible to determine how much of the oxide involves Ni incorporation. However, some areas of the examined samples show weak signals of Ni and/or Fe incorporation both on the surface and in cross-section. The best understanding of these data is that the spinel forms concurrently with the simple oxides and is only able to form when there is sufficient concentration of Ni or Fe in the reacting fluid and when the original metal is exposed (otherwise the diffusion through the oxide film will substantially reduce the spinel formation rate).

During continued exposure in deoxygenated water, the oxide film remains rather thin, as with TiN, and both CrO_2 and Cr_2O_3 form since the oxidation process is quite slow (note that only ~40 nm of oxide is grown on the Cr surface). Under ideal conditions, this would mean that both the Cr and CrN are chemically protective. However, only the Cr was found to be protective, indicating mechanical instability of CrN or failure in a manner similar to that suggested for TiN in the previous section except that the entire coating does not oxidize (i.e, defect removal followed by interface destabilization acts concurrent with spallation due to poor adhesion).

In the presence of oxygen, the likely explanation is less straightforward due to the dissolution of the formed oxides. Comparing the Cr and CrN samples, it is clear that Cr oxidized much more quickly (the entire coating was oxidized in NWC and most of it was oxidized 350°C with 1ppm O₂), and also loses mass more quickly than CrN. Given the greater spallation of CrN compared to Cr in the absence of oxygen, it would be expected that CrN should lose mass more quickly than Cr in the presence of oxygen, which is the reverse of what happens. It is suggested that this inversion of expectations is caused by the rate at which Cr oxidizes.

Through pitting and coating defect attack, the faster reaction rate with respect to oxygen will result in the complete oxidation of the coating to the interface. At that point the SiC would become oxidized and any penetration of water via crack or other defect will be able to dissolve the SiO₂ and thus delaminate the coating. Such interfacial oxidation is observed in Cr, but far less so and only at edges in CrN. Therefore, the mass loss of CrN is suggested to be caused only by dissolution of Cr_xO_y following its formation and through the already operating spallation mechanisms. However it must still be addressed that the CrN attack rate is far greater in oxygen than outside of it and significant thickness is not lost in the bulk. The increased mass loss may be explained by the increased attack of Ti-containing macroparticles combined with cracking along Ti layers leading to destabilization of the coating. This will operate in deoxygenated conditions, but the enhanced reactivity of the macroparticles to oxygen will likely accelerate this process (not to mention the enhanced interface destabilization if the interface becomes exposed).

The next section discusses the irradiation-induced failure modes. Recommendations for coating improvement are reserved for that discussion.

6.6 MITR Exposures of Coated SiC

6.6.1 Cavity and Lattice Swelling

Under irradiation below 800°C, SiC is known to swell with a strong dependence on temperature as a consequence of radiation-induced point defects [21, 37, 226]. Near 300°C SiC swelling saturates to about 1.8% volume by 0.1-1 dpa. As shown in Figure 4.48, the present MITR irradiation results on lattice parameter swelling are in full agreement with these literature findings.

Such data are not available for most of the coating materials. Radiation effects studies on pure Cr are sparse, and existing literature relied on low energy ion irradiation, likely subject to surface and/or implantation zone effects, preventing conclusive swelling behavior from being known [227-229]. However, Cr has a melting point of ~1900°C [128], corresponding to an absolute temperature $T/T_m = 0.26$ at 300°C. As Cr has a BCC structure, void swelling is expected to onset at an earlier homologous temperature than FCC materials [230]. Therefore, the observed void swelling in this work is expected. The ceramic coatings behave somewhat differently than expected in this regime. The point-defect-induced swelling of SiC suggests a potentially similar effect for TiN and CrN. However, neither was observed to have significant change in the lattice parameter, nor was void formation observed. In the TiN, the high melting point ($T_m = 2950^\circ\text{C}$ [128]) suggests a $T/T_m = 0.18$, which is well below the homologous temperature expected for swelling in an FCC-like structure [230, 231]. Thus, the lack of void formation in TiN is

consistent with expectations. Whether the lack of any lattice swelling is due to the intrinsic material or the presence of significant impurities was not evaluated by this study and will need to be explored in future work. Finally, CrN decomposes near 1000°C [128, 232] and may be expected to therefore form voids under the conditions investigated by this work. Since none are observed in this work, void formation in CrN may be suppressed by impurities or the homologous temperature may not be a meaningful metric to evaluate the temperatures at which ceramics which under thermal decomposition will swell.

6.6.2 Cracking/Delamination under Dry Irradiation

No microstructural or other physical effects of irradiation were observed on TiN coatings, regardless of substrate type. While this lack of radiation-induced changes is in principle a positive observation, this result may be specific for the TiN coating used in this study because the TiN phase has a broad composition range with stable vacancy structures [233]. The chemical composition analysis in Table 1 implies that the material was hyperstoichiometric, which is expected to cause a different response to neutron irradiation than would be expected for stoichiometric TiN, similar to observations of ZrC_x [234]. Moreover, significant concentrations of carbon and oxygen impurities (~5 at.% in total) may also affect the microstructural stability under irradiation but were not apparent at the damage level investigated in this study.

Unlike TiN, the first-generation monolithic CrN, multilayer CrN/Cr, and Cr coatings experienced irradiation-induced cracking within the coating and/or debonding at the interfaces of the coating and substrate. Such cracking is a concern for cladding applications as it will potentially result in a loss of hermeticity of the coated SiC system once a network of cracks and pores has formed. The cracks may also accelerate hydrothermal corrosion of the coating under normal operating conditions. These results suggest that these first-generation coating systems need to be improved for use in irradiation environments. Naturally, it is also possible that these material systems are poor candidates for the application. However, it should be emphasized that these samples may not be representative of the best performance from these systems due to the significant amount of the impurities and lack of processing optimizations. Thus, this study does not by itself invalidate these materials as coatings on SiC for ATF cladding.

Differential substrate-coating irradiation-induced swelling is a possible source of the irradiation-induced cracking, debonding, and crack deflection at the relevant coating-substrate interfaces. This phenomenon is a common challenge for the interface between SiC and a dissimilar material under irradiation, as observed in irradiated SiC joints with interlayers [58]. The lattice expansion due to irradiation (Figure 4.48) can be used to quantify the volumetric swelling of the coatings and the substrates for cases where cavity swelling does not occur. It has been demonstrated that the volume expansion of SiC, quantified from the XRD analysis, is comparable to the macroscopic swelling for irradiation conditions similar to this study [235]. The XRD analysis obtained a lattice expansion of ~0.55% (corresponding to 1.7% volumetric swelling) in the monolithic CVD SiC materials. That degree of swelling is similar to the 0.65% length change following irradiation at 300°C to 0.5 dpa reported in ref. [236]. The present XRD results showed a negligible lattice parameter changes for the coatings due to irradiation. In addition, microstructural characterizations did not find any indication of other dimensional changes,

including phase transformations and formations of dislocation loops or voids that possess size and/or density large enough to contribute to macroscopic swelling. Therefore, the cracks propagating perpendicular to the coating interface in Figure 4.51 can potentially be explained by tensile stresses resulting from larger swelling of the SiC substrate than the coatings. The interfacial debonding may occur when the vertical crack is deflected at the interface or the coating adhesion is relatively weak.

Assuming homogeneous swelling within the coating and substrate materials, a simple equation to estimate the coating strain due to differential irradiation swelling ($\epsilon_{C,irr}$) can be derived for the cases where the coating thickness is much smaller than the substrate thickness [237].

$$\epsilon_{C,irr} = \frac{\Delta L_S - \Delta L_C}{1 - \nu_C + \frac{2t_C E_C}{t_S E_S} (1 - \nu_S)} \approx \frac{\Delta L_S - \Delta L_C}{1 - \nu_C} \quad \text{Eqn. 6.18}$$

where ΔL indicates fractional length change caused by irradiation swelling, t is material thickness, E is Young's modulus, and ν is Poisson's ratio. In equation 2, the subscripts C and S represent coating and substrate, respectively. Note that a positive $\epsilon_{C,irr}$ indicates tensile strain in the coating. Considering also the coating residual stresses given in Table 4 and stresses induced from lattice mismatch, the maximum coating and elastic stress in operation can be estimated using Eqn. 6.19

$$\sigma_C = \frac{E_C}{1 - \nu_C} \left[\Delta L_S - \Delta L_C + \int_{T_{room}}^{T_{operate}} (\alpha_S - \alpha_C) dT \right] + \sigma_{res} \quad \text{Eqn. 6.19}$$

where, α_S and α_C are the CTE functions of substrate and coating, respectively, integrated from the room to operating temperatures, and σ_{res} is the residual stress in the coating at room temperature. Using these equations, three stresses are estimated for the coatings and given in Table 6.3. It should be noted that the foregoing is representative of the maximum stress and strain. Due to irradiation creep, the actual values will creep towards zero with increasing exposure. However, the maximum stresses will drive the cracking and delamination process and is thus still relevant in the present evaluations. As shown in the experimental section, all coatings but the Cr were in compression at room temperature. Because all the coatings have larger CTE's than SiC, cooling from the deposition temperature induces tensile stresses, not compressive ones, implying the deposition process (high velocity particles impacting the target) induces significant compression. Moreover the CTE mismatch requires that upon heating to the operational temperature compressive stresses are induced, increasing compression of the ceramics and placing the Cr in slight compression (100 MPa). Differential swelling from irradiation reduces this compressive stress in two of the coating systems and induces a medium to large tensile stress to the Cr. Cooling introduces a large tensile stress component and all coatings remain in tension while at room temperature.

This post-testing room temperature stress corresponds to maximum strains of between 0.2% and 0.7% in each coating and could conceivably explain some of the cracking observed. Moreover, it implies that the TiN should probably have also cracked, while it did not. However, two caveats must be considered. First, the CTE values for these specific coatings were not determined.

Table 6.3: Stress estimates (in GPa) at the coating interfaces following heating from room temperature to 300°C (column 1), then following the swelling of the SiC by neutron irradiation (column 2), and finally after cooling back down to room temperature (column 3).

<i>Coating</i>	<i>Residual stress (MPa, from Table 3.10)</i>	<i>Stress after heating to 300°C</i>	<i>Stress at 300°C with neutron-induced SiC swelling</i>	<i>Stress at room temperature following reactor exposure</i>
<i>Cr</i>	0.22	-0.1	1.8	2.1
<i>CrN/Cr multilayer</i>	-0.60	-1.4	0.3	1.1
<i>CrN</i>	-1.28	-2.1	-0.3	0.4
<i>TiN</i>	-1.66	-3.5	-0.4	1.3

Rather, literature values were used. As these coatings are non-stoichiometric with significant impurities, the exact amount of CTE swelling is not known. Second, although the differential swelling appeared significant, irradiation creep may compete, moderating the swelling-induced strains [238]. The magnitude of irradiation creep strain of metals could become comparable to the observed length change of irradiated SiC [239-241]. However, the quantitative values of the creep compliance coefficient for irradiated Cr, CrN, and TiN are not known. In general, the processes of simultaneous stress buildup due to differential swelling and stress relief by irradiation creep are expected to be complicated. In the case of the Cr coating, this could lead to the coating absorbing the swelling-induced strain over time.

The Ti and Ni interlayers could theoretically have served to reduce swelling-induced strain by plastic deformation. However, there was no obvious benefit from the Ni interlayer in the Cr-coated CMC specimen based on the surface crack observations (Figure 4.50). It is possible that the Ni layer was not ductile due to process-induced impurities, irradiation-induced damage, and/or nuclear transmutation events. On the other hand, comparison of the crack density between two types of CrN-based coating (i.e., the monolithic CrN with the Ti layer and multilayer CrN/Cr with the Ni interlayer) implies that the presence of the Ti layer may have been beneficial for minimizing surface cracks. However, since these two coatings did not have the same composition, thickness, or vendor definitive conclusions on this point are not made in this study. This result warrants further investigation of the effects of Ti or another ductile interlayer on the crack resistance. The interlayer also enables modification of the residual stress in the coating [237]. Controlling compressive residual stress in the coating will be key to absorbing swelling-induced strain.

The use of a ductile coating is another approach for mitigation of cracking by differential swelling. Ductility of Cr depends on impurity elements [242, 243], strain rate [244], and testing environment [244]. Matsumoto et al. conducted a comprehensive study on fracture behavior of 99.88% pure Cr under various environments [244]. The findings conclude that Cr is ductile even at room temperature under relatively low strain rate mechanical tests. In addition, the failure strain was more than 10% at ~300°C. These results suggest that Cr-based coating might be resistant to the swelling-induced strain of 0.7–0.8 %. The Cr coating in this study contained ~10 atm.% of impurity elements, which likely degrades ductility. The ductility is also likely degraded by irradiation at low doses [245-247]. The effect of the void formation (Figure 4.52) on embrittlement must be evaluated as the significant impact of voids on failure mode found in [248].

6.6.3 Effects of Radiation in PWR Water

None of the coatings were successful in the presence of a water coolant during irradiation. The multilayer CrN/Cr coating spalled in all three conditions (in the core, above the core with no radiation damage, and out-of the core where it was shielded from gamma and neutron effects). Thus, the CrN coatings must be made more adherent, possibly with ductility-enhancements as discussed in the previous sections, prior to deployment. Since no monolithic CrN was included in the wet exposure, its intrinsic aqueous corrosion behavior is not known.

The Cr (on CVD SiC) samples were significantly more protective, oxidizing slightly in both the out-of-core and above-core (radiolysis-affected) regions of the loop. Following irradiation, however, substantial spallation is evident both from the mass change and from the optical and SEM micrographs Figure 4.61 and Figure 4.62. This is consistent with the substantial cracking of Cr highlighted in section 4.1. Improvement in the ductility of the Cr, especially on the interface, may solve this problem. If the overall swelling is not severe enough as to substantially embrittle the Cr, with further development Cr may become a viable coating system.

Unlike with the CVD substrate, Cr coated on the CMC samples lost mass in all MITR conditions. In the water-only and radiolysis-affected regions, the mass loss was rather small, but increased by nearly an order of magnitude for the MITR in-core sample with the addition of radiation damage and core-radiolysis. The link between radiation damage and coating spallation has already been discussed. A possible explanation for the observed spallation in the above-core and out-of-core regions is that local spallation occurred where Cr was directly deposited on fibers (such as on an edge of the CMC tube which had been cut and thus had exposed fibers prior to deposition). The CMCs used in this study were initially overcoated and then cut into sections with no additional overcoat. When the Cr was applied, therefore, one or both ends would have been coated directly onto exposed fibers and may not have been hermetically sealed. Subsequent SiC swelling would have further opened these cracks, exposing the SiC interior while also potentially delaminating isolated Cr deposits.

The final coating system, TiN, appeared to be protective and adherent in both radiation-damage-free conditions (above-core and out-of core). Oxide formation was further rather limited as shown in Figure 4.58. However, the entire coating was either consumed or spalled for the in-core sample. As the coating did not appear to be altered by radiation damage in the first section of this study, this effect was not expected. Four possible explanations are suggested.

First, the specific coating exposed in the core may have spalled due to abnormal defects from the coating process (thus rendering the in-core coating not comparable to the other samples exposed). This explanation is unlikely as it would not likely have caused the entire coating to be removed with no trace on the surface. Rather, some local spallation may have been observed. Second, the corrosion of TiN may have been significantly accelerated by the order of magnitude higher radiolysis products in the core, compared to the above core region. Prior work has shown TiN has some susceptibility to oxidation-induced spallation in aggressive environments [51, 107], lending some credibility to this idea. Third, TiN, as a ceramic, may be subject to the same point-defect effects on corrosion chemistry as other ceramics such as SiC. Kondo et al, and Maeda et al [91, 214, 215] reported substantial increases in the corrosion of SiC as a result of radiation damage alone. Maeda et al [214] further linked the corrosion to changes in the electrochemistry caused by point defects in the SiC. It may be that TiN is especially susceptible to such effects, and as such becomes chemically unstable by rapid oxidation in the presence of radiation damage. Finally, as this coating system was non-stoichiometric and contained a lot of impurities, the failure may be due to the chemistry of the coating and will be corrected upon changes in the coating chemistry. Testing these hypotheses is beyond the scope of this work and is reserved for future study.

Chapter 7: Summary and Conclusions

Because SiC is a major contender to replace Zr-based alloys as an accident-tolerant nuclear fuel cladding, the long-term hydrothermal corrosion of SiC at normal operating conditions is of considerable interest to the academic community as well as the nuclear industry at large. This work examined the aqueous corrosion behavior of coated and uncoated SiC (high purity monolithic as well as CVD composite) in the presence and absence of irradiation.

Two sets of scoping tests were used to down-select coating materials and understand how impurities will affect the corrosion of SiC in LWR-like conditions near 300°C. Uncoated SiC was found to corrode slowly and linearly when the resistivity was high or the water oxygen concentration was low. For low resistivity (doped) samples, oxygen attacked grain boundaries and led to significant grain fallout. No passivating SiO₂ film was formed to mitigate corrosion, consistent with prior work. Moreover, monolithic Al₂O₃, a major sintering aid in high density sintered SiC, was found to recede at a rate of >0.1mm/yr, far beyond what is acceptable for nuclear fuel cladding. Sintered SiC must be protected with either a sufficiently thick high resistivity CVD SiC overcoat and/or a corrosion mitigation coating. Several materials ZrN, NiCr, Ni, Cr, TiN, and CrN were initially explored as coating options on CVD SiC. NiCr and ZrN were poorly adherent, while Ni had too high of a neutron absorption cross-section. Therefore, these latter coating materials were deferred for consideration under a different study. The remaining materials, Cr, TiN, and CrN were explored further with high resistivity CVD SiC in autoclave and reactor environments.

CVD SiC was exposed to high purity compressed water in conditions spanning the temperature range of 288-350°C, with 1-4 wppm O₂ or 0.15-3 wppm H₂. The general equation,

$$\text{Rate} \left[\frac{\text{mg}}{\text{cm}^2\text{s}} \right] = 0.1458 T \left(1.09(1 - 10^{-3}T)[\text{O}_2]e^{-\frac{1.275 \times 10^4}{T}} + 7.91 \times 10^{-6}e^{-\frac{7.39 \times 10^3}{T}} \right) \text{ was}$$

developed to predict the uniform corrosion of SiC. In the absence of oxygen, SiC was found to corrode with very little grain boundary attack. However, in the presence of oxygen, grain boundaries are aggressively attacked and fallout of small grains is evident in the mass change data in as little as a few hundred hours at 350°C, or in a few thousand hours at 288°C. It was suggested that SiC reacts through a single dominant activation step with water and a single dominant activation step with oxygen in water. However, it was noted that with respect to water the analysis is low confidence due to the low magnitude (and relatively high error) of the corrosion rate. Comparison with other data sets suggested that use of high temperature tests with B and Li additions may have significant effects on the corrosion of SiC. However, the effects are reserved for a future study.

Moreover, polishing was observed to have a significant effect in oxygenated conditions. This is attributed to the excess area (compared to projected area) and early grain fallout. The additional roughness was suggested to necessitate shorter overall grain boundaries at peaks and valleys, leading to early grain fallout (compared to a polished, flat sample). In deoxygenated conditions, no boundary attack was observed so this mechanism could not operate. Moreover, the magnitude of the mass loss was quite low (especially compared to experimental error) and there was no significant effect of the additional area, within the error. It is recommended that SiC samples be

polished carefully in corrosion experiments to obtain a more accurate corrosion values. After 5 years at 320°C in deoxygenated water, it is expected that SiC will have lost a thickness of $\sim 1.3\mu\text{m}$, well within the expected acceptable limits. As the effects of Li and B on SiC corrosion above 300°C are in question, these must also be resolved prior to deployment of SiC as an ATF cladding.

The effects of radiation were partially evaluated using the in-reactor autoclave for 166 days at the MIT Nuclear Reactor Laboratory in PWR-simulating water chemistry. Samples were placed at three exposure locations: in, above, and out-of the reactor core, corresponding to ~ 1 dpa of neutron damage and an energy deposition rate of $\sim 1.4\text{kGy/s}$, 0 dpa and $\sim 36\text{Gy/s}$, and 0 Gy/s, respectively in each condition. A Python script was developed to evaluate the radiolysis products at each location. It was found that peroxide concentrations were approximately an order of magnitude higher in the core than above it, while SiC corroded at a rate of only 2-4x times faster in the core than above it, making a deconvolution of the radiation damage and radiolysis product effects impossible in this study.

In the core, the corrosion rate of high resistivity SiC was low enough that the extrapolated 5-year recession in the core was a maximum of 4 μm . Moreover, localized attack over this 127 day period was minimal and will not likely lead to excessive grain fallout over the cladding lifetime. CMC SiC corroded much faster. This additional corrosion was attributed to the exposure of fibers and fiber-matrix interphases interior to the CMC as a consequence of cutting the tubes during preparation. Thus, CMCs will require a thick, hermetic, CVD overcoat to be viable for 5-year use. Moreover, the lack of a passivating film of SiO_2 on such an overcoat during normal operation suggests that a hermetic overcoat is prudent. For example, if a crack were to develop in the SiC overcoat, no self-healing of the SiC would be possible, fission gases would have a chance to escape, and the fiber-matrix interphase would be susceptible to attack.

The coatings retained from the scoping tests for this hermetic sealing purpose were also investigated in the above conditions with the addition of an irradiation to 0.5 dpa (neutron fluence ($E > 0.1$ MeV) of $8.3 \times 10^{24} \text{ n/m}^2$) at 270-340°C in Ar. This exploratory study was intended to acquire better understanding of irradiation effects in the candidate coating systems in the absence of water corrosion. In Ar, all coatings except the TiN cracked substantially. The Cr and multilayer CrN/Cr coatings cracked the most. Voids formed in the Cr coating with an approximate swelling of 0.2%, as expected given the absolute temperature relative to the melting temperature. It is reserved for a future study to determine the extent of this swelling and whether it may provide a benefit or a drawback to the coating's viability.

Beyond these observations, SEM, TEM, and XRD analyses revealed no radiation-induced changes in the coatings apart from cracks, implying the cracking resulted from irradiation-induced swelling of the underlying SiC that induced tensile strains in the coatings. This cracking resulted in failure of the coatings when exposed to water (except for the monolithic CrN, which was not exposed). A Ti compatibility layer in the monolithic CrN appeared to minimize the crack density in that coating. While the TiN coating did not crack in the presence of radiation, it was fully removed from the substrate during the in-core exposure to water, implying that radiation

sensitizes this TiN coating to corrosion, similar to SiC. However, it was noted that the order-of-magnitude higher peroxide concentration in the core compared to the above-core region was such that the source of the enhanced TiN degradation, radiation damage versus peroxide attack, could not be identified in this work.

These results are similar to the ORNL autoclave exposures. In deoxygenated conditions, the TiN and CrN spalled substantially, while the Cr was protective. Spallation was attributed to defects during the coating process, particularly at engraving marks or other potentially shadowed regions, and enhanced oxidation at edges, leading to destabilization of the coating. In the presence of oxygen, all the coatings failed quickly.

TiN oxidized rapidly and spalled from the surface. While its oxide (TiO_2) is stable in water under all conditions, it did not remain on the surface following oxidation. This implies that a combination of effects may have led to failure. 1) defects during the coating process or caused by sample handling, as with the deoxygenated conditions, could lead to spallation. 2) after exposure of the interface, the SiC can oxidize and the SiO_2 product dissolve, delaminating the coating.

These same processes also apply to the Cr and CrN coatings. The multilayer Cr/CrN coating was found to spall immediately and requires significant adjustment for any further use. The nominally monolithic CrN was found to have a very thin Ti-compatibility layer at the SiC interface, along with a few thin Ti layers dispersed through the coating. Due to this, Ti macroparticles were common all through the coating, sometimes spanning it.

Although in the CrO_2 and Cr_2O_3 products formed during exposure are not stable in the conditions studied, they were observed at the edges but were not observed at sample center in large quantities. It is thus suggested that the oxidation rate of CrN far from edges dominates the corrosion rate, while near edges, the additional stresses lead to enhanced oxidation, causing the oxide dissolution rates to govern the overall coating corrosion rate. Further, it was found that the Ti macroparticles oxidized quickly and partial delamination of the coating occurred beginning at these particles with cracks occasionally propagating along the additional Ti interlayers. By removing these additional interlayers and reducing or eliminating the macroparticles, this “monolithic” CrN has significant potential as a corrosion-resistant coating.

The Cr coating oxidized significantly faster than the CrN. In addition to the formation of CrO_2 and Cr_2O_3 , pitting of the coating surface underneath the oxide commonly occurred. Moreover, upon exposure to the autoclave fluid, the interface oxidized rapidly and delaminated. This was suggested to be a significant mechanism for failure. Unlike the CrN, the dissolution of Cr-oxides is likely the rate limiting step in oxygenated conditions and many regions with only Cr-oxides were observed on the SiC surface.

Elemental analysis revealed the CrN and TiN coatings were non-stoichiometric and all coatings contained ~5% C and O impurities, likely compromising ductility and potentially causing radiation stability hazards at time frames beyond the current study. For use in LWRs on SiC/SiC fuel cladding, it is suggested that these coatings be developed with more compressive residual stresses (to mitigate the differential swelling with respect to the SiC), more ductility (by doping

or with compatibility layers), and/or lower impurity concentrations. Moreover, the extent of swelling in the Cr requires further evaluation as a vector for embrittlement.

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APPENDICES

APPENDIX A: REPORTED OPTICAL SAMPLE IMAGING

A.1 HCL Scoping Tests

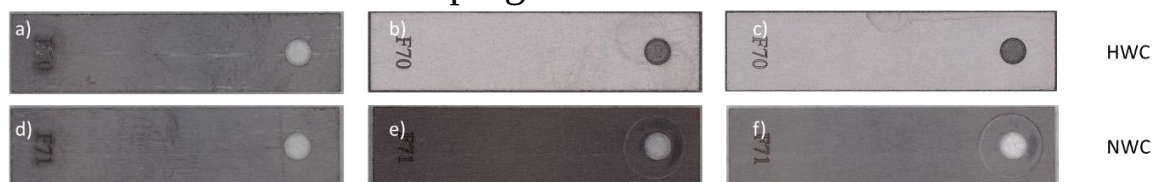


Figure A. 1. Pictures of pure, high resistivity CVD SiC at a) 0h, b) 200h, and c) 400h of exposure in a BWR-HWC (2880C, 150ppb H₂) environment and d) 0h, e) 200h, and f) 400h of exposure to the BWR-NWC (2880C, 2ppm O₂) environment.



Figure A. 2: Pictures of pure CMC SiC from Hypertherm at a) 0h, b) 200h, and c) 400h of exposure in a BWR-HWC (288°C, 150ppb H₂) environment and d) 0h, e) 200h, and f) 400h of exposure to the BWR-NWC (288°C, 2ppm O₂) environment.



Figure A. 3: Pictures of pure CMC SiC from NGNP at a) 0h, b) 200h, and c) 400 h of exposure in a BWR-HWC (288°C, 150ppb H₂) environment and d) 0h, e) 200h, and f) 400h of exposure to the BWR-NWC (288°C, 2ppm O₂) environment.

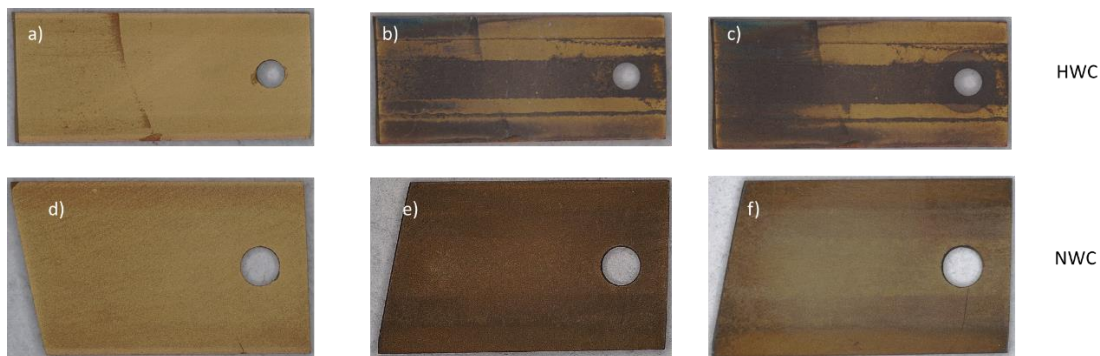


Figure A. 4: Pictures of pure TiN at a) 0h, b) 200h, and c) 400 h of exposure in a BWR-HWC (288°C, 150ppb H₂) environment and d) 0h, e) 200h, and f) 400h of exposure to the BWR-NWC (288°C, 2ppm O₂) environment.



Figure A. 5: Pictures of pure Cr at a) 0h, b) 200h, and c) 400 h of exposure in a BWR-HWC (288°C, 150ppb H₂) environment and d) 0h, e) 200h, and f) 400h of exposure to the BWR-NWC (288°C, 2ppm O₂) environment.



Figure A. 6: Pictures of Cr-coated CMC SiC at a) 200h, and b) 400 h of exposure in a BWR-HWC (288°C, 150ppb H₂) environment. No sample was included in the BWR-NWC (288°C, 2ppm O₂) environment.

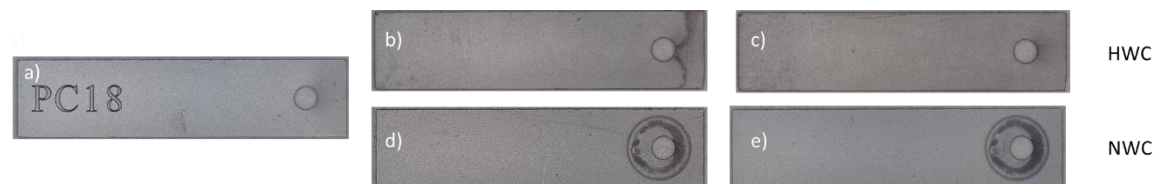


Figure A. 7: Pictures of Cr-coated CVD SiC at a) 0h, and b) 200h, c) 400h of exposure in BWR-HWC (288°C, 150ppb H₂) environment and d) 200h and e) 400h of exposure in BWR-NWC (288°C, 2ppm O₂) environment.



Figure A. 8: Pictures of pure CrN-coated CVD SiC at a) 0h, b) 200h, and c) 400 h of exposure in a BWR-HWC (288°C, 150ppb H₂) environment and d) 0h, e) 200h, and f) 400h of exposure to the BWR-NWC (288°C, 2ppm O₂) environment.

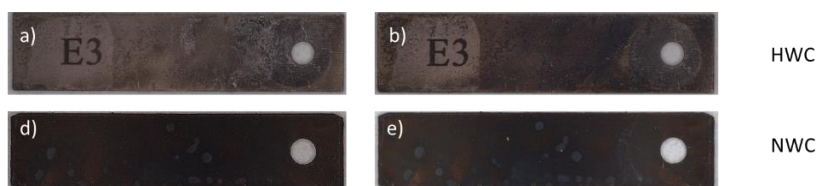


Figure A. 9: Pictures of Ni-coated CVD SiC at a) 200h, and b) 400h of exposure in a BWR-HWC (2880C, 150ppb H₂) environment and d) 200h, and e) 400h of exposure to the BWR-NWC (288°C, 2ppm O₂) environment.

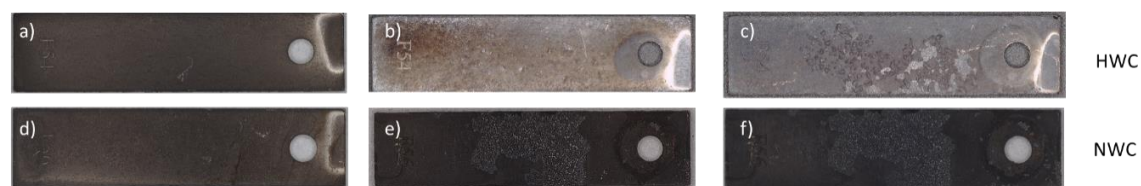


Figure A. 10: Pictures of NiCr-coated CVD SiC at a) 0h, b) 200h, and c) 400 h of exposure in a BWR-HWC (2880C, 150ppb H₂) environment and d) 0h, e) 200h, and f) 400h of exposure to the BWR-NWC (288°C, 2ppm O₂) environment.



Figure A. 11: Pictures of TiN-coated CVD SiC at a) 0h, b) 200h, and c) 400 h of exposure in a BWR-HWC (288°C, 150ppb H₂) environment and d) 0h, e) 200h, and f) 400h of exposure to the BWR-NWC (288°C, 2ppm O₂) environment.

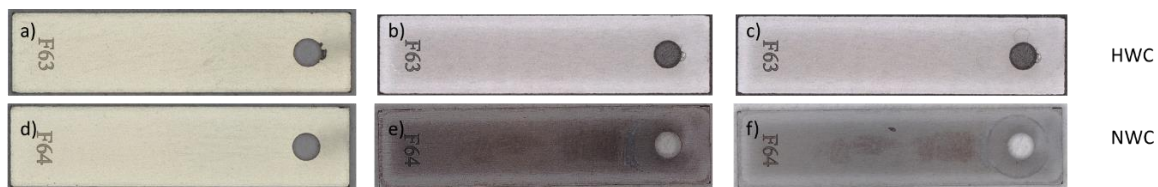


Figure A. 12: Pictures of ZrN-coated CVD SiC at a) 0h, b) 200h, and c) 400 h of exposure in a BWR-HWC (2880C, 150ppb H₂) environment and d) 0h, e) 200h, and f) 400h of exposure to the BWR-NWC (2880C, 2ppm O₂) environment.

A.2 Coating Images from HCL Full Tests

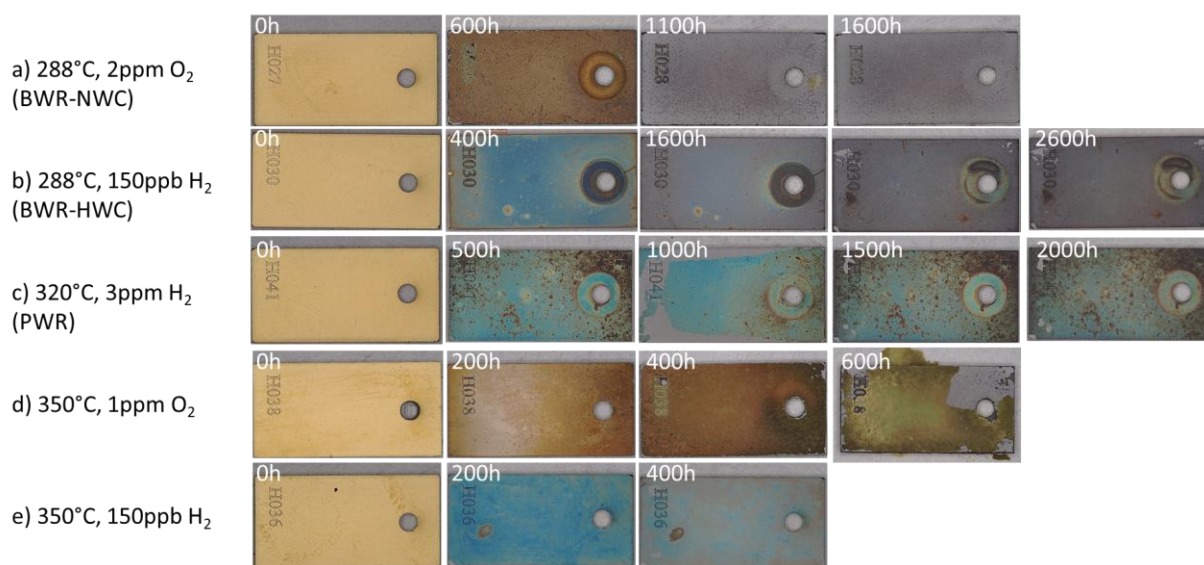


Figure A. 13: Pictures of TiN coated on CVD SiC specimens and exposed to a) BWR-NWC (2ppm O₂, 288°C), b) BWR-HWC (150ppb H₂, 288°C), c) PWR (3ppm H₂, 320°C), d) 350°C with 1ppm O₂, and e) 350°C, with 150ppb H₂ for exposure times as noted in the images.

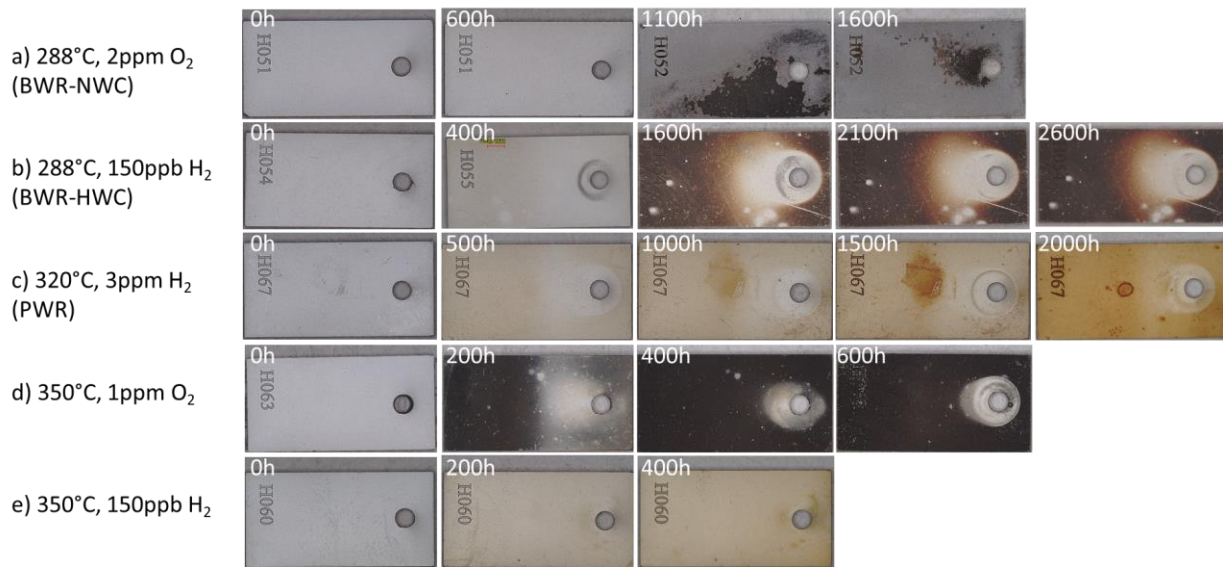


Figure A. 14: Pictures of Cr coated on CVD SiC specimens and exposed to a) BWR-NWC (2ppm O₂, 288°C), b) BWR-HWC (150ppb H₂, 288°C), c) PWR (3ppm H₂, 320°C), d) 350°C with 1ppm O₂, and e) 350°C, with 150ppb H₂ for exposure times as noted in the images.

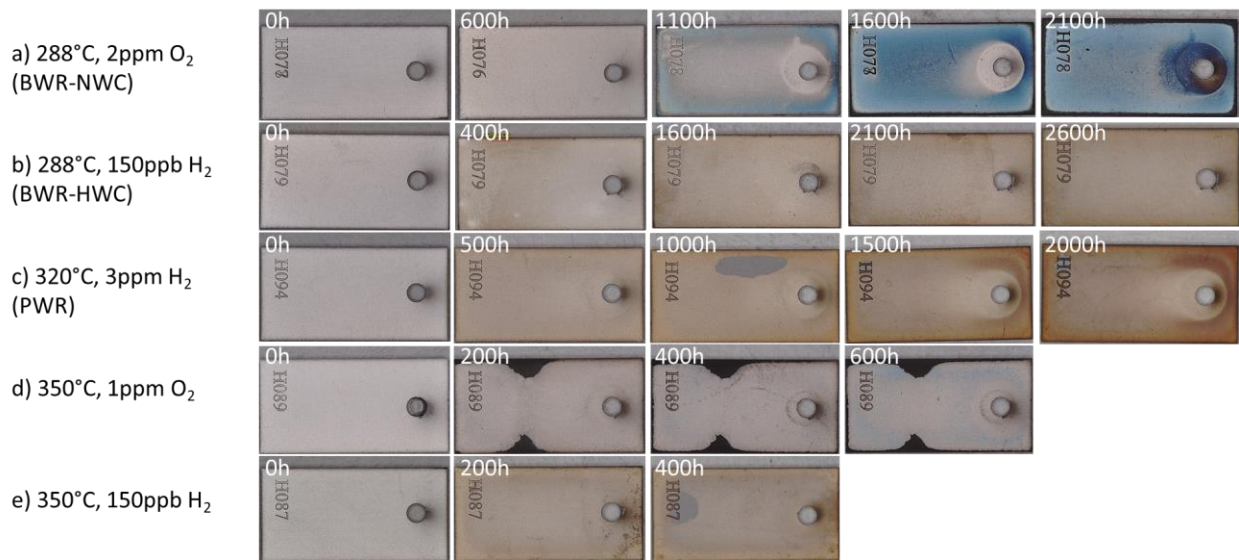


Figure A. 15: Pictures of monolithic CrN coated on CVD SiC specimens and exposed a) BWR-NWC (2ppm O₂, 288°C), b) BWR-HWC (150ppb H₂, 288°C), c) PWR (3ppm H₂, 320°C), d) 350°C with 1ppm O₂, and e) 350°C, with 150ppb H₂ for exposure times as noted in the images.

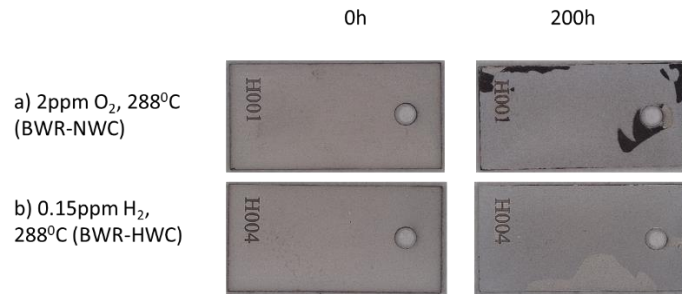


Figure A. 16: Pictures of multilayer Cr/CrN coated on CVD SiC specimens and exposed to a) BWR-NWC (2ppm O₂, 288°C), and b) BWR-HWC (150ppb H₂, 288°C) for 0, 200, 400, and 600h, as noted in the images.

**APPENDIX B:
OPTICAL IMAGES OF MITR-IRRADIATED
SAMPLES**

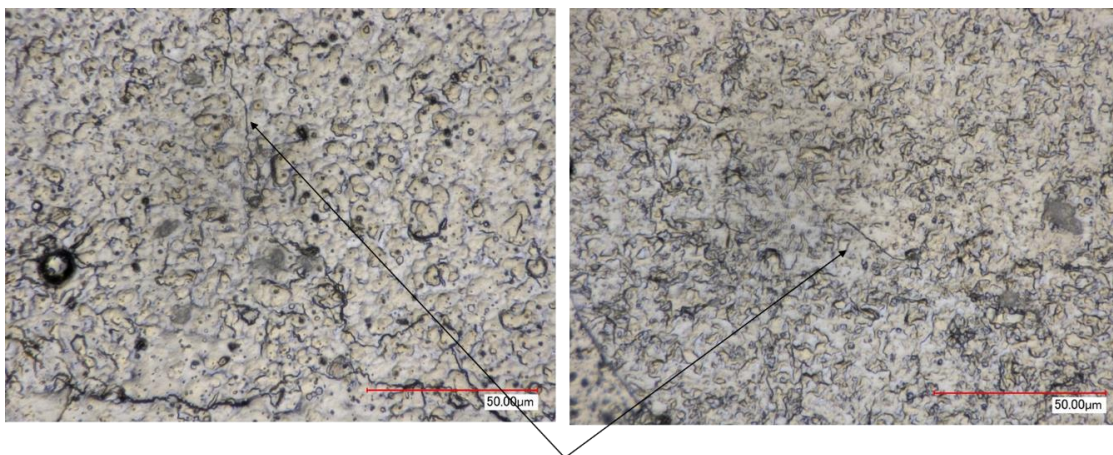


Figure B. 1: Photographs of cracking in TM-CrN coatings on high resistivity CVD SiC. Cracks are indicated with the black arrows.

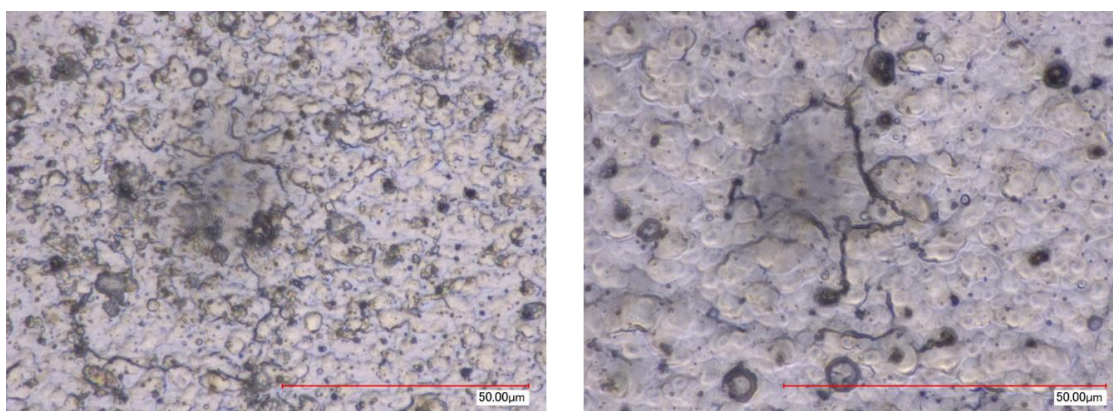


Figure B. 2: Photographs of cracking in TM-CrN coatings on high resistivity CVD SiC, with a Ni compatibility layer.

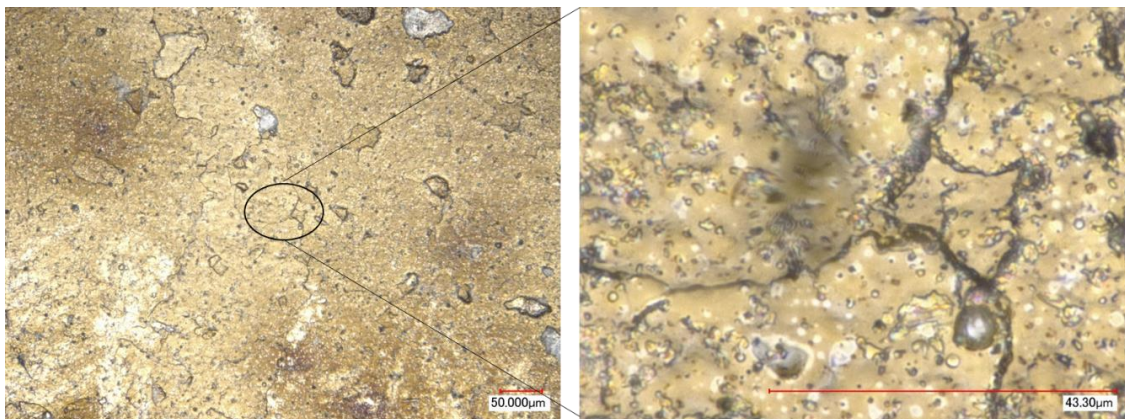


Figure B. 3: Photographs of TM-CrN coatings on low resistivity CVD SiC. Some cracks observed coming from surface defects.

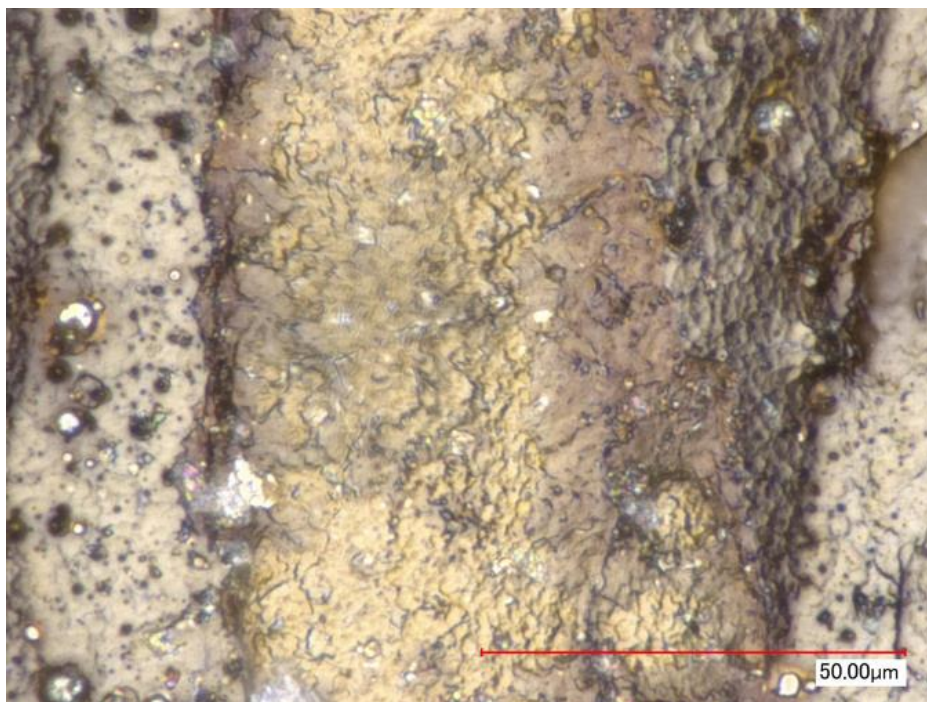


Figure B. 4: Photographs of CrN coatings on CMC SiC. No cracks observed.

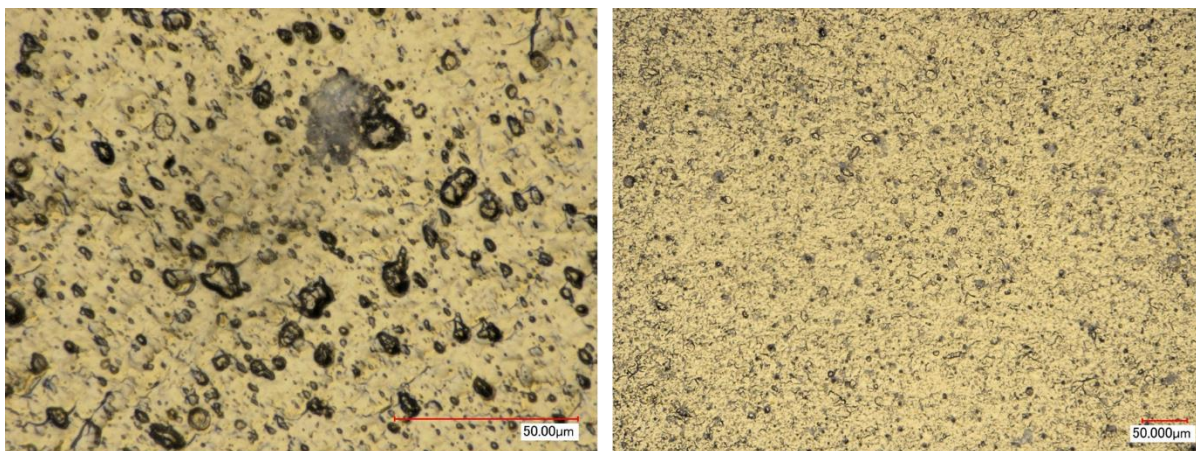


Figure B. 5: Photographs of TiN coatings on CVD SiC. No cracks observed.

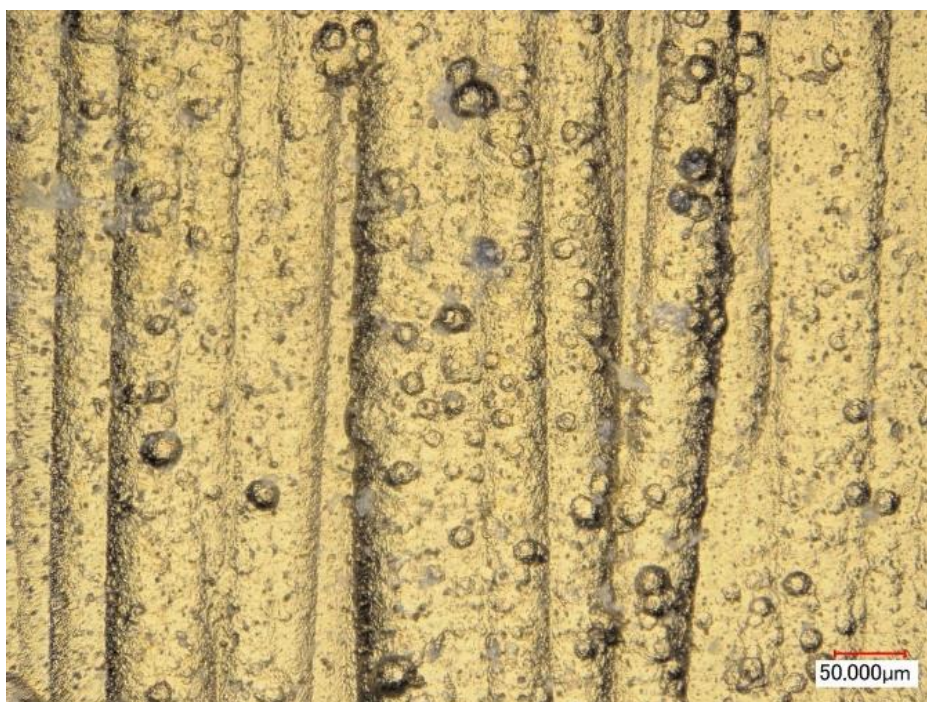


Figure B. 6: Photographs of TiN coatings on CMC SiC. Few noticeable cracks observed.

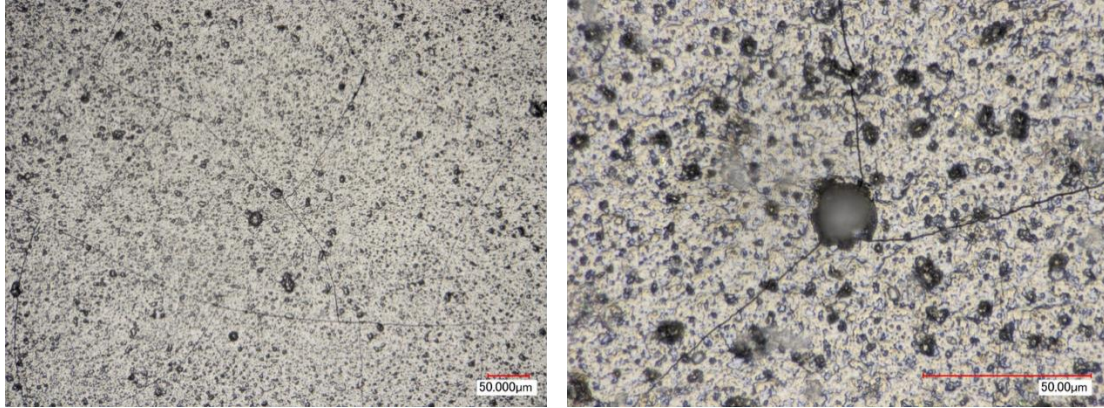


Figure B. 7: Photographs of multilayer Cr/CrN coatings on high resistivity CVD SiC. Extensive cracking is observed.

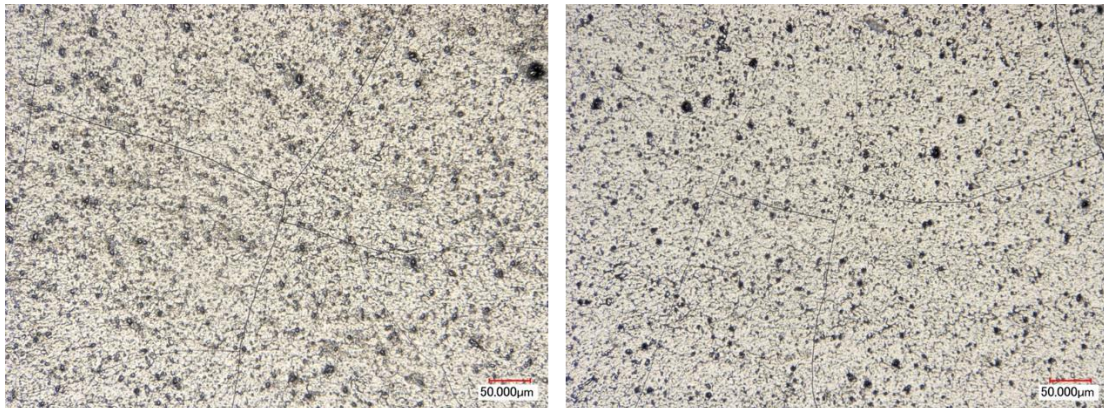


Figure B. 8: Photographs of multilayer Cr/CrN coatings on high resistivity CVD SiC with a Ni compatibility coating. Extensive cracking is observed.

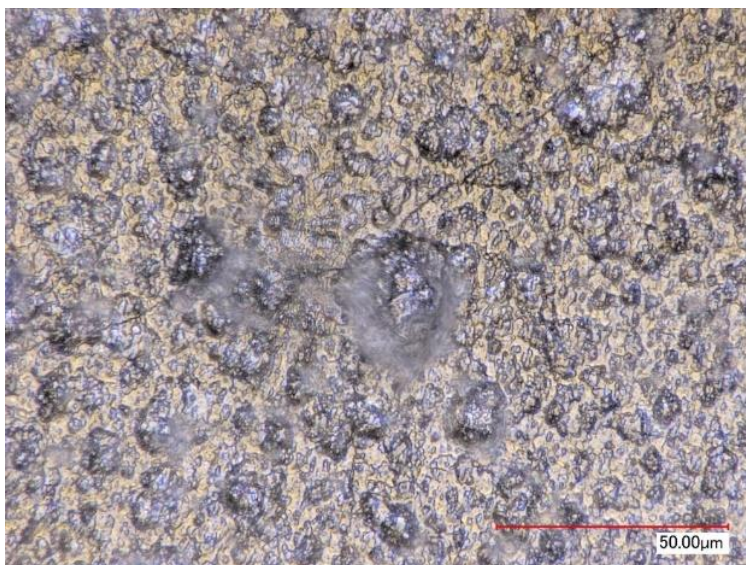


Figure B. 9: Photographs of multilayer Cr coating on high resistivity CVD SiC. Limited cracking is observed.

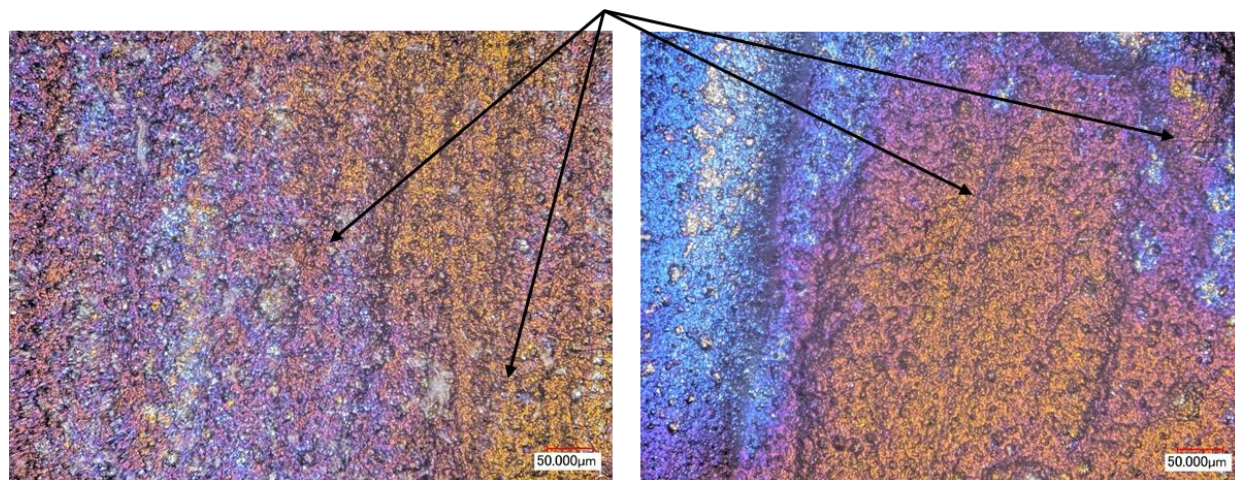


Figure B. 10: Photographs of multilayer Cr coating on CMC SiC. Extensive cracking is observed on the surface.

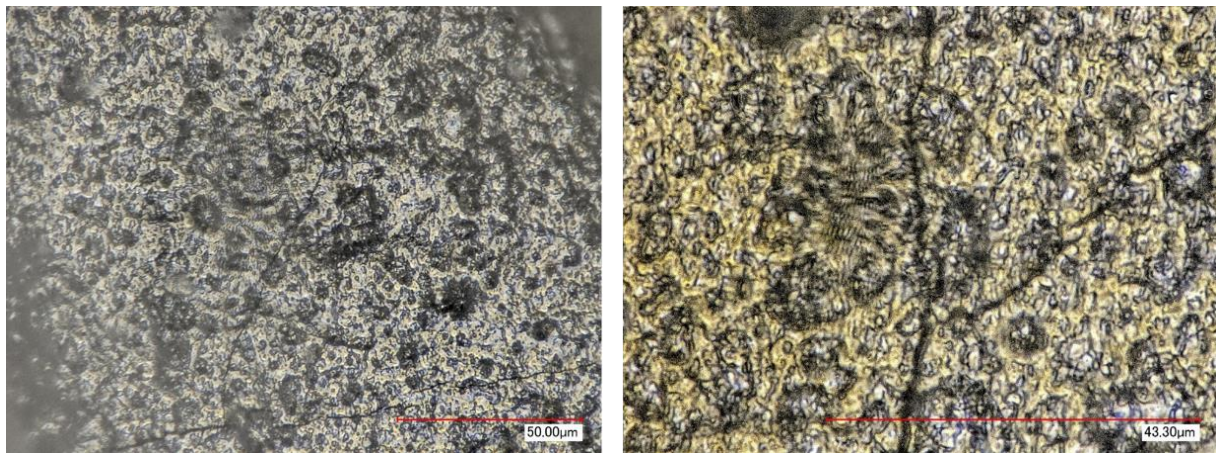


Figure B. 11: Photographs of multilayer Cr coating on CMC SiC with a Ni compatibility layer. Extensive cracking is observed on the surface.

APPENDIX C:
SCRIPT FOR THE EVALUATION OF RADIOLYSIS
PRODUCTS

```

1  # THIS ROUTINE COMPUTES THE TIME-DEPENDENT CONCENTRATIONS OF SPECIES IN A HOMOGENEOUS SYSTEM.
2  # IT IS FORMATTED FOR RADIOLYSIS CAUSED BY UP TO 2 RADIATION SOURCES (NEUTRON AND GAMMA).
3  # A PROPERLY FORMATTED INPUT FILE IS REQUIRED BUT THE FOLLOWING PARAMETERS MAY NEED TO BE
4  # CHANGED IN THE ROUTINE BELOW
5  # THIS ROUTINE TOGETHER WITH ALL THE INPUT AND OUTPUT FILES FOR THIS WORK CAN BE FOUND AT
6  # https://trace.tennessee.edu/utk\_nuclpubs/5/
7  #   autobalance    ... True if the following arrays will be computed from the input file
8  #                   if autobalance is false, the following must be explicitly supplied. The input file must still include the componentlist
9  #line
10 #   componentlist  ... list of chemical componenets in the system
11 #   material balance arrays:
12 #       atom_count ... number of atoms in each species
13 #       H_count    ... number of hydrogens in each species
14 #       O_count    ... number of oxygens in in each species
15 #
16 #       neg        ... value of the negative charge (0 for non-negative species)
17 #       pos        ... value of positive charge (0 for non-positive species)
18 #   Red           ... for reducers, weight to apply to the species (0 for non-reducers)
19 #   oxid          ... for oxidizers, weight to apply to the species (0 for non-oxidizers)
20 #   name          ... name of input file to draw from
21 #   buffer        ... array corresponding to elements of componentlist. Where 0 the concentrations are allowed to vary. Where 1 the
22 #concentration is held constant
23 #   abtol         ... absolute concentration tolerance for the solver
24 #   tStart        ... power of ten to scale the output as a function of time. Time is scaled back to 0, so this number does not affect the
25 #output, only output locations
26 #   number        ... total number of outputs
27 #   sequentialfiles ... if True, multiply files (in name) will be run sequentially. That is, the initial concentration of the next run will
28 #be the final concentration of the current run
29 # ALL OF THE ABOVE VARIABLES ARE INCLUDED AT THE TOP OF THE SECOND SECTION.
30 # DEFAULT INPUTS (AND INPUT SCRIPTS) ARE RELEVANT FOR THE ASSOCIATED PUBLICATION WHERE THE
31 # DETAILS OF THIS MODEL ARE DESCRIBED
32 # THE FIRST SECTION DEFINES ALL FUNCTIONS, THE SECOND SETS UP THE PROBLEM, THE THIRD AND FOURTH
33 # SECTIONS RUN PROBLEM AND OUTPUT ITS RESULTS IN A VARIETY OF FILES

```

```

34
35 import math as m
36 import sys
37 import numpy as np
38 from scipy.integrate import solve_ivp
39 import os
40 #-----
41 -----
42 """ Define concentration differential functions
43
44 def Conc_Delta(t,Conc):
45     Rate = FindRates(Conc)
46     delta = np.empty([r_end+1])
47     i = 0
48     while i <= r_end:
49         if (buffer[i]):
50             delta[i] = 0
51         else:
52             delta[i]= np.sum(np.multiply(Rate,Coeffsfull[0:,i]))+P[i]
53         i += 1
54     return delta
55
56 def FindRates(Conc):
57     Rates = np.multiply(k,np.ma.prod(Conc**CoeffsRate,axis = 1))
58     return Rates
59
60 def BuildReactions():
61     ReactionList = np.empty_like(k,dtype =np.dtype('U50'))
62
63     i = 0
64     while i <= k_end:
65         Reactlist =np.empty_like(componentlist,dtype = np.dtype('U25'))
66         Ri = 0

```

```

67 Prodlist = np.empty_like(componentlist, dtype = np.dtype('U25'))
68 Pi = 0
69
70 # collect products and reactants into lists
71 j = 0
72 while j <= r_end:
73     if(Coeffs[i,j]==-1): # reactant with order 1
74         Reactlist[Ri] = componentlist[j]
75         Ri += 1
76     elif (Coeffs[i,j] <= -2): # reactant with order > 1
77         Reactlist[Ri] = "{0:s}" .format(componentlist[j])
78         ii = -2
79         while (ii >= Coeffs[i,j]):
80             Reactlist[Ri] += " + {0:s}" .format(componentlist[j])
81             ii -= 1
82         Ri += 1
83     elif (int(Coeffs[i,j]) != Coeffs[i,j]): # non-integer species
84         if(Coeffs[i,j] > 0):
85             Prodlist[Pi] = "{0:0.3f} {1:s}" .format(Coeffs[i,j], componentlist[j])
86             Pi += 1
87         elif(Coeffs[i,j] < 0):
88             Reactlist[Ri] = "{0:0.3f} {1:s}" .format(Coeffs[i,j], componentlist[j])
89             Ri += 1
90     elif (Coeffs[i,j] == 1): # product of order 1
91         Prodlist[Pi] = componentlist[j]
92         Pi += 1
93     elif (Coeffs[i,j] >= 2): # product of order > 1
94         Prodlist[Pi] = "{0:s}" .format(componentlist[j])
95         ii = 2
96         while (ii <= Coeffs[i,j]):
97             Prodlist[Pi] += " + {0:s}" .format(componentlist[j])
98             ii += 1
99         Pi += 1

```

```

100         j += 1
101
102     # build reaction string
103     j = 0 # build reactat side of the reaction string for reaction i
104     ReactionList[i] = Reactlist[j]
105     while j < 10:
106         j += 1
107         if(Reactlist[j]): # add a reactant
108             ReactionList[i] += " + "+Reactlist[j]
109         else: # end of reactant stream
110             ReactionList[i] += " = "
111         j = 10
112     j = 0 # build product side of the reaction string for reaction i
113     ReactionList[i] += Prodlist[j]
114     while j < 10:
115         j += 1
116         if(Prodlist[j]): # add a product
117             ReactionList[i] += " + "+Prodlist[j]
118         else: # end of reaction
119             j = 10
120     i += 1
121     return ReactionList
122
123 def BuildDifferentials():
124     DifferentialList = np.zeros_like(Cinit,dtype =np.dtype('U500'))
125     i = 0 # loop over all species
126     while (i<=r_end):
127         DifferentialList[i] = "d("+componentlist[i]+") / d(t) = " # differential (left) side
128         tempstring = "
129         j =0
130         while (j<=k_end): # right side
131             if (Coeffsfull[j,i]):
132                 if(tempstring): # add extra term if one is already there

```

```

133     tempstring += " + "
134     # rate constant and concentration change of species i per reaction
135     if (Coeffsfull[j,i] == int(Coeffsfull[j,i])): # integer coefficients
136         if (Coeffsfull[j,i] < 0):
137             tempstring += "({0:1.0f})*k{1:1.0f}".format(Coeffsfull[j,i],j+1)
138         elif(Coeffsfull[j,i] == 1):
139             tempstring += "k{0:1.0f}".format(j+1)
140         else:
141             tempstring += "{0:1.0f}*k{1:1.0f}".format(Coeffsfull[j,i],j+1)
142     else: # float coefficients
143         if (Coeffsfull[j,i] < 0):
144             tempstring += "({0:1.3f})*k{1:1.0f}".format(Coeffsfull[j,i],j+1)
145         else:
146             tempstring += "{0:1.3f}*k{1:1.0f}".format(Coeffsfull[j,i],j+1)
147     # add in concentration factors from all reactants
148     ii = 0
149     while (ii <=r_end):
150         if(CoeffsRate[j,ii]):
151             if(CoeffsRate[j,ii] == 1):
152                 tempstring += "*" + str(componentlist[ii])
153             elif(CoeffsRate[j,ii] == int(CoeffsRate[j,ii])):
154                 tempstring += "{0!s}^{1:1.0f}".format(componentlist[ii],CoeffsRate[j,ii])
155             else:
156                 tempstring += "{0!s}^{1:5.5f}".format(componentlist[ii],CoeffsRate[j,ii])
157             ii += 1
158     j += 1
159     # add right side of equation and external production term
160     DifferentialList[i] += tempstring + ' + P{0:s}'.format(componentlist[i])
161     i += 1
162     return DifferentialList
163
164 def ObtainComponents():
165     # this uses the first line of the input file to obtain all molecules of interest

```

```

166 inputs = open(name[filenum]+" .txt", "r")
167 line = inputs.readline()
168 endpoint = line.find('#')-1
169 if (endpoint < 0):
170     componentlist = np.array(line.split(), dtype = str)
171 else:
172     componentlist = np.array(line[0:endpoint].split(), dtype = str)
173 inputs.close()
174 listlen = len(componentlist)
175
176 # get locations of H and H2O components and number of atoms in each component for mass balance
177 neg = np.zeros_like(componentlist, dtype = float)
178 pos = np.zeros_like(componentlist, dtype = float)
179 H_count = np.zeros_like(componentlist, dtype = float)
180 O_count = np.zeros_like(componentlist, dtype = float)
181 atom_count = np.zeros_like(componentlist, dtype = float)
182 i = 0
183 H2O_loc = -1
184 H_loc = -1
185 while i < listlen:
186     if (componentlist[i] == 'H2O'):
187         H2O_loc = i
188     elif (componentlist[i] == 'H'):
189         H_loc = i
190     if (componentlist[i] == "e" or componentlist[i] == "e_aq" or componentlist[i] == "e-" or componentlist[i] == "e_aq-"
191         or componentlist[i] == "eq" or componentlist[i] == "eq-"):
192         neg[i] = 1
193     else:
194         el = componentlist[i]
195         j = 0
196         while j < len(el):
197             if (el[j] == 'H'): # update count of hydrogens
198                 try:

```

```

199         H_count[i] = int(el[j+1])
200         j += 1
201     except:
202         H_count[i] = 1
203     elif (el[j] == 'O'): # update oxygen count
204         try:
205             O_count[i] = int(el[j+1])
206             j += 1
207         except:
208             O_count[i] = 1
209     elif (el[j] == "-" or el[j] == "m"): # update negative charges
210         neg[i] = 1
211     elif (el[j] == "+" or el[j] == "p"): # update positive charges
212         pos[i] = 1
213     else:
214         print('An unsupported element or designation. {0:s}.is being used in the species {1:s}'.format(el[j],el))
215         print('Auto mass and charge balance only supports hydrogen and oxygen counting designated as "H" or "O",
216 respectively')
217         print('with single negative or positive charges on any species designated by any of "-", "m", "+", and "p"')
218         print('electrons may also be included as various vesions of "e_aq"\n')
219         j += 1
220     i += 1
221     atom_count = H_count+O_count
222     if (H_loc == -1):
223         sys.exit('no "H" species included. This is required for correct G-value assignment.\nThe program will terminate')
224     if (H2O_loc == -1):
225         sys.exit('no "H2O" species included. Water is needed for material balance.\nThe program will terminate')
226
227     return [componentlist, atom_count, H_count, O_count, neg, pos, H_loc, H2O_loc]
228
229 def RxnAnalyzer(errorstring, MajorError):
230     # analyzes each reaction for internal balance in charge, redox, and mass. Also finds location of water decomposition
231     O_bal = np.zeros_like(k)

```

```

232 H_bal = np.zeros_like(k)
233 at_bal = np.zeros_like(k)
234 C_bal = np.zeros_like(k)
235 Redox_bal = np.zeros_like(k)
236 charge = pos-neg
237 redox = Red-oxid
238 errors = False
239 decompeval = False
240 decomp = -1
241 terror = '    MAJOR ERROR: The following reactions were out of balance as indicated:\n'
242 i = 0
243 while i <= k_end: # loop over all reactions
244     O_bal[i] = np.sum(np.multiply(Coeffsfull[i,:],O_count))
245     H_bal[i] = np.sum(np.multiply(Coeffsfull[i,:],H_count))
246     at_bal[i] = np.sum(np.multiply(Coeffsfull[i,:],atom_count))
247     C_bal[i] = np.sum(np.multiply(Coeffsfull[i,:],charge))
248     Redox_bal[i] = np.sum(np.multiply(Coeffsfull[i,:],redox))
249     if(O_bal[i] or H_bal[i] or at_bal[i] or C_bal[i] or Redox_bal[i]):
250         terror+= '    {0!s} with k = {1:1.3e}: '.format(i+1,k[i])
251         if (O_bal[i]):
252             terror += ' Oxygen change of {0:2.0f};'.format(O_bal[i])
253         if (H_bal[i]):
254             terror += ' Hydrogen change of {0:2.0f};'.format(H_bal[i])
255         if (at_bal[i]):
256             terror += ' Net mass change of {0:2.0f};'.format(at_bal[i])
257         if (C_bal[i]):
258             terror += ' Charge change of {0:2.0f};'.format(C_bal[i])
259         if (Redox_bal[i]):
260             terror += ' Redox imbalance of {0:2.0f};'.format(O_bal[i])
261         errors = True
262         terror += '\n'
263     if (CoeffsRate[i,H2O_loc] == 1 and not(decompeval)): # find H2O = H+ + OH-
264         decompeval = True

```

```

265     j = 0
266     while (j <= r_end):
267         if (componentlist[j] == "Hp" or componentlist[j] == "H+" or componentlist[j] == "OH-" or componentlist[j] == "OHm"):
268             if(Coeffsfull[i,j] != 1):
269                 decompeval = False
270             elif(j != H2O_loc):
271                 if(Coeffsfull[i,j] != 0):
272                     decompeval = False
273             j += 1
274         if (decompeval):
275             temp = i
276         i += 1
277     if (decompeval):
278         decomp = temp
279     else:
280         buffer[H2O_loc]= 1
281         Cinit[H2O_loc] =1
282         errorstring += '    The decomposition of water in H+ and OH- was not detected. \n    The initial concentration of water was
283 been set to 1 and buffered\n'
284         if (errors):
285             errorstring += terror
286             MajorError =True
287         else:
288             errorstring += '    All reactions are balanced\n'
289         return [decomp, decompeval,MajorError, errorstring]
290 #-----
291 -----
292 #%% VARIABLE ASSIGNMENTS
293
294 # USER-DEFINABLE VARIABLES
295 autobalance = True # True if componentlist will be obtained from inputs and used to populate the following arrays
296     # if autobalance is false, componentlist, H_count, O_count, H2O_loc, H_loc, at_count, neg, and pos must all be supplied here
297 Red = np.array([0,1,0,1,0,0,2,0,0,0,0,0,0]) # reducer power coefficients, this is NOT determined automatically

```

```

298 oxid = np.array([0,0,0,0,1,0,0,2,3,2,1,4,3,5]) # oxidizer power coefficients, this is NOT determined automatically
299 buffer = np.array([0,0,0,0,0,0,0,0,0,0,0,0,0,0]) # 0 if concentration is allowed to vary, 1 if held constant
300 abtol = 1E-19# absolute tolerance for solver.
301 reltol = 1E-7 #relative tolerance for solver. Errors are kept to <= abtol + reltol*abs(solution)
302 tStart = -7 # power of ten, resulting units of seconds. This is used for scaling only
303 number = 100 # number of output points, logarithmically distributed
304 suffix = "_decomp1_vvhigh" # suffix to add to name elements
305 name = ["Radiolysis-Core"+suffix,"Radiolysis-Above"+suffix,"Radiolysis-Decay"+suffix]
306 sequentialfiles = True # True if each file should use the previous file's final concentrations as initial inputs.
307         # All other information will be taken from the input file (i.e, k values, reactions, etc will not be from first file)
308 # END USER-DEFINABLE VARIABLES.
309
310 # load and unpack input data
311 MajorError = False
312 filenum = 0
313 while filenum < len(name): # loop over all input decks
314     if(autobalance):
315         [componentlist, atom_count, H_count, O_count, neg, pos, H_loc, H2O_loc] = ObtainComponents()
316         errorstring = "
317         Data = np.loadtxt(name[filenum]+".txt",skiprows = 1)
318         k = Data[3:,0]
319         if (filenum and sequentialfiles): # if using sequential files and at least one file has been run, use previous file results for
320 concentrations
321             Cinit = solution.y[:,solsize-1]
322         else:
323             Cinit = Data[2,1:] # first run or if non-sequential files are used
324         i = 0
325         Ciniterr =False
326         while (i<len(Cinit)):
327             if (Cinit[i]<0):
328                 errorstring += '    MAJOR ERROR: Initial concentration of component {0:s} is less than zero (=
329 {1:5.3e})\n'.format(componentlist[i],Cinit[i])
330                 MajorError = True

```

```

331     Ciniterr = True
332     i += 1
333     if not(Ciniterr):
334         errorstring += '    Initial concentrations are valid (>= 0)\n'
335     tStop = m.log10(Data[2,0])
336     G_g = Data[0,1:]
337     G_n = Data[1,1:]
338     D_g = Data[0,0]
339     D_n = Data[1,0]
340     Coeffs = Data[3:,1:]
341     k_end = len(Coeffs[0:,0])-1
342     r_end = len(Coeffs[0,:])-1
343     rho = Cinit[H2O_loc]/1000.*18 # g/cm^3, assumes water is
344     redox0 = np.sum(np.multiply(Cinit,Red))-np.sum(np.multiply(Cinit,oxid))
345
346     # Set up problem
347     Reactions = BuildReactions()
348     Coeffsfull = Coeffs
349     CoeffsRate = np.zeros_like(Coeffs)
350     j = 0 # build coefficients to build the individual reaction rates
351     while j <= k_end:
352         i = 0
353         while i <= r_end:
354             if (Coeffs[j,i]>=0):
355                 CoeffsRate[j,i] = 0
356             else:
357                 CoeffsRate[j,i] = -Coeffs[j,i] # negative values indicate reactants
358             i += 1
359         j += 1
360     [decomp, decompeval, MajorError,errorstring] = RxnAnalyzer(errorstring,MajorError)
361     CoeffsRate[:,H2O_loc] = 0
362     if (decompeval):
363         CoeffsRate[decomp,H2O_loc] = 1 # water decomposition reaction. Water does not contribute to other reactions

```

```

364     # production values from irradiation
365     P = 1.0364E-7*rho*(D_g*G_g+D_n*G_n) # set net production
366     P[H2O_loc] = -np.sum(np.multiply(O_count,P)) # adjust production of H and H2O for accurate mass balance
367     errorstring += '    Production rate of H as input = {0:1.3e} M/s. It was adjusted by {1:1.3e} M/s to '.format(P[H_loc], -
368 np.sum(np.multiply(P,H_count)))
369     P[H_loc] += -np.sum(np.multiply(P,H_count))
370     errorstring += '{0:1.3e} M/s\n'.format(P[H_loc])
371     k[40] = 1e4
372     #-----
373     -----
374     #%% Differential equation evaluations
375     t = np.logspace(tStart,tStop,number)
376     tsize = len(t)
377
378     # solve system
379     solution = solve_ivp(Conc_Delta, [t[0], t[tsize-1]],Cinit, method='BDF',t_eval =t, atol = abtol, rtol = reltol)
380     solution.t -= 10**tStart # scale time to 0
381     # determine concentration deltas at each time point
382     i = 0
383     dC_s1 = np.array(solution.y)
384     solsize =len(solution.y[0,:])
385     while (i<=solsize-1):
386         dC_s1[:,i] = Conc_Delta(solution.t,solution.y[0:,i])
387         i += 1
388
389     #-----
390     -----
391     #%% Write out results
392
393     # Set up and populate remainng output arrays for material balances
394     solutionout = np.insert(solution.y,0,solution.t,0)
395     dC_s1 = np.insert(dC_s1,0,solution.t,0)
396     at_count = np.empty(solsize)

```

```

397 redox = np.empty(solsize)
398 charge = np.empty(solsize)
399 i = 0
400 while i < solsize:
401     at_count[i] = np.sum(np.multiply(solutionout[1:,i],atom_count))
402     red1 = np.sum(np.multiply(solutionout[1:,i],Red))-redox0
403     ox1 = np.sum(np.multiply(solutionout[1:,i],oxid))
404     redox[i] = np.sum(np.multiply(solutionout[1:,i],Red))-np.sum(np.multiply(solutionout[1:,i],oxid))-redox0
405     charge[i] = np.sum(np.multiply(solutionout[1:,i],pos))-np.sum(np.multiply(solutionout[1:,i],neg))
406     i += 1
407 solutionout = np.insert(solutionout,0,at_count,0)
408 solutionout = np.insert(solutionout,0,redox,0)
409 solutionout = np.insert(solutionout,0,charge,0)
410
411 # check for errors and update log
412 i = 0
413 negcheck = 0
414 terrorstring = '    Negative concentration errors at t = \n'
415 while (i < solsize):
416     j = 0
417     while (j < r_end):
418         if (solution.y[j,i] < 0):
419             negcheck += 1
420             terrorstring += '    {0:5.3e} seconds for component {1:s}. C =
421 {2:5.3e}\n'.format(solution.t[i],componentlist[j],solution.y[j,i])
422             j += 1
423         i += 1
424     if (negcheck):
425         terrorstring += '    TOTAL NUMBER OF CONCENTRATION ERRORS = {0:5.0f}\n'.format(negcheck)
426     else:
427         terrorstring = '    The solution contains no negative concentrations\n'
428     errorstring += terrorstring
429     if (at_count[solsize-1]-at_count[0]): # atomic balance

```

```

430     errorstring += '    The mass balance changed by {0:1.3e} atomic M across the run\n'.format(at_count[solsize-1]-at_count[0])
431 else:
432     errorstring += '    There was no change in the total number of atoms across the run\n'
433 if (redox[solsize-1]-redox[0]): # redox balance
434     errorstring += '    The redox balance changed by {0:1.3e} M across the run\n'.format(redox[solsize-1]-redox[0])
435 else:
436     errorstring += '    There was no change in the redox balance across the run\n'
437 if (charge[solsize-1]-charge[0]): # charge balance
438     errorstring += '    The charge balance changed by {0:1.3e} M across the run\n'.format(charge[solsize-1]-charge[0])
439 else:
440     errorstring += '    There was no change in the charge balance across the run\n'
441
442 # Write the primary results file
443 componentlist_fmt = np.empty_like(componentlist)
444 i = 0
445 while i < len(componentlist):
446     componentlist[i] = componentlist[i].ljust(13,' ')
447     i += 1
448 solutionfile = open(name[filenum]+"_Results.txt","w+")
449 # dose and G-values
450 if(MajorError):
451     solutionfile.write('NOTE: ONE OR MORE MAJOR ERRORS WERE DETECTED. SEE THE NOICE AND ERROR LOG AT
452 THE END OF THE SOLUTION OUTPUT FOR DETAILS\n')
453     solutionfile.write('Input G-values for each species are below. Production rates for H2O and H are assigned by material balance
454 rather than G-values\n')
455     solutionfile.write('G-values are in units of molecules/100eV and the production rates are in units of M/s\n')
456     solutionfile.write('%s %1.3e %s\n' % ("Gamma Dose Rate = ",D_g," in Gy/s"))
457     solutionfile.write('%s %1.3e %s\n' % ("Neutron Dose Rate = ",D_n," in Gy/s"))
458     solutionfile.write("G_neutron, G_gamma, Production Rates\n")
459     for i in range(len(G_n)):
460         solutionfile.write('%1.3e, %1.3e, %1.3e, %s\n' %(G_n[i],G_g[i],P[i],componentlist[i]))
461 # mass balance and concentrations
462 solutionfile.write("pos-neg,  reduc-oxid, tot_at,  time (s) , ")

```

```

463 np.savetxt(solutionfile,componentlist, fmt = '%s    ',delimiter = ',',newline = ',')
464 solutionfile.write("\n")
465 np.savetxt(solutionfile, np.transpose(solutionout), fmt = '%+5.3e', delimiter = ',',newline = '\n')
466 solutionfile.write("pos-neg,  reduc-oxid, tot_at,  time (s) , ")
467 np.savetxt(solutionfile,componentlist, fmt = '%s    ',delimiter = ',',newline = ',')
468 # final concentration flux at final time step
469 solutionfile.write("\n          Final Concentration Flux:  ")
470 np.savetxt(solutionfile, dC_s1[1:,solsize-1], fmt = '%+5.3e',newline = ',')
471 # C(tf)-C(t0)
472 solutionfile.write("\n          Final-Initial Concentration: ")
473 np.savetxt(solutionfile, solutionout[4:,solsize-1]-solutionout[4:,0], fmt = '%+5.3e',newline = ',')
474 # print list of any and all negative concentration terms in the solution
475 solutionfile.write("\n\nSolution Notice and Error Log:\n")
476 solutionfile.write('{0:s}'.format(errorstring))
477 # individual reactions and rate constants with reaction rates at initial and final times
478 solutionfile.write("\nInitial Rate(1/s) Final Rate(1/s) k (1/M/s or 1/s)  Associated Reaction:\n")
479 InitRate = FindRates(Cinit)
480 FinRate = FindRates(solution.y[:,solsize-1])
481 out_k = np.empty_like(k,dtype = 'U200')
482 i = 0
483 while (i<=k_end):
484     out_k[i] = '{0:5.3e}      {1:5.3e}      {2:5.3e}      {3:s}'.format(InitRate[i],FinRate[i],k[i],Reactions[i])
485     i += 1
486 np.savetxt(solutionfile,out_k, fmt = '%s',newline = '\n')
487 solutionfile.close()
488
489 # Print file of concentration fluxes
490 solutionfile = open(name[filenum]+"_Conc_Delta.txt","w+")
491 solutionfile.write("time (s) , ")
492 np.savetxt(solutionfile,componentlist, fmt = '%s    ',delimiter = ',',newline = ',')
493 solutionfile.write("\n")
494 np.savetxt(solutionfile, np.transpose(dC_s1), fmt = '%+5.3e',newline = '\n')
495 solutionfile.close()

```

```

496
497 # Print assembled equations and data formatted for Polymath input
498 space = ('\n')
499 i = 0
500 while i <= r_end: # strip trailing spaces and replace "-" and "+" with "m" and "p"
501     componentlist[i] = componentlist[i].rstrip()
502     componentlist[i] = componentlist[i].replace("-", "m")
503     componentlist[i] = componentlist[i].replace("+", "p")
504     i += 1
505 differentials = BuildDifferentials()
506 differentialsfile = open(name[filenum]+"_Assembly.txt", "w+")
507 i = 0
508 while i <= r_end: # differential equations
509     differentialsfile.write(differentials[i]+"\n")
510     i += 1
511 differentialsfile.write(space)
512 i = 0
513 while i <= k_end: # rate constants
514     differentialsfile.write('k{0:s} = {1:5.3e}\n'.format(i+1, k[i]))
515     i += 1
516 differentialsfile.write(space)
517 i = 0
518 while i <= r_end: # G-values from neutrons
519     differentialsfile.write('G_n{0:s} = {1:5.3e}'.format(componentlist[i], G_n[i]))
520     i += 1
521 differentialsfile.write(space)
522 differentialsfile.write(space)
523 i = 0
524 while i <= r_end: # G-values from gamma
525     differentialsfile.write('G_g{0:s} = {1:5.3e}\n'.format(componentlist[i], G_g[i]))
526     i += 1
527 differentialsfile.write(space)
528 i = 0

```

```

529 H2Olist = 'PH2O = -('
530 Hlist = 'PH = -2*PH2O-('
531 Ocounter = 0
532 Hcounter = 0
533 while i<=r_end: # Production equations
534     if (i != H2O_loc and i != H_loc):
535         differentialsfile.write('P{0:s} = 1.0364E-7*rho*(D_g*G_g{0:s}+D_n*G_n{0:s})\n'.format(componentlist[i]))
536         if(O_count[i]):
537             if(Ocounter):
538                 H2Olist += ' + '
539             if(O_count[i] == 1):
540                 H2Olist += 'P{0:s}'.format(componentlist[i])
541             else:
542                 H2Olist += '{0:1.0f}*P{1:s}'.format(O_count[i],componentlist[i])
543             Ocounter += 1
544         if(H_count[i]):
545             if(Hcounter):
546                 Hlist += ' + '
547             if(H_count[i] == 1):
548                 Hlist += 'P{0:s}'.format(componentlist[i])
549             else:
550                 Hlist += '{0:1.0f}*P{1:s}'.format(H_count[i],componentlist[i])
551             Hcounter += 1
552         i += 1
553     differentialsfile.write('{0:s})\n'.format(H2Olist))
554     differentialsfile.write('{0:s})\n'.format(Hlist))
555     differentialsfile.write(space)
556     i = 0
557     while i<=r_end: # initial concentrations
558         differentialsfile.write('{0:s}(0) = {1:5.3e}\n'.format(componentlist[i],Cinit[i]))
559         i += 1
560     # gamma and neutron dose with intial and final times
561     differentialsfile.write('rho = {0:1.5f}\n'.format(rho))

```

```
562 differentialsfile.write('D_g = {0!s}\n'.format(D_g))
563 differentialsfile.write('D_n = {0!s}\n'.format(D_n))
564 differentialsfile.write('t(0) = {0!s}\n'.format(10**tStart))
565 differentialsfile.write('t(f) = {0!s}\n'.format(10**tStop))
566 differentialsfile.close()
567
568 if(MajorError):
569     print ("NOTE: AT LEAST ONE MAJOR ERROR WAS DETECTED. SEE THE '..._Results.txt' FILE FOR DETAILS\n")
570     print('Run number {0:1.0f} complete using the following input file: "{1:s}"'.format(filenum+1,name[filenum]))
571     filenum += 1 # update file number for sequential runs
572
```

APPENDIX D:
SUPPLEMENTARY KINETICS ANALYSIS
REGARDING THE CORROSION OF UNCOATED SiC
IN THE MITR WATER EXPOSURE

D.1 Mass change and error analysis

Mass data presented in the article was evaluated in the following way in the preparation of the figures. Weight change was calculated via Eqn D.1,

$$dm = \frac{m_f - m_i}{SA \, dt} \quad \text{Eqn D.1}$$

Where m_f and m_i are the final and initial average masses measured, SA is the sample surface area, and dt is the hot exposure time. Standard error propagation was used to assign approximate error to each data point using equation Eqn D.2,

$$\sigma_{dm} = |dm| \sqrt{\left(\frac{\sqrt{\sigma_{m_f}^2 + \sigma_{m_i}^2}}{dm} \right)^2 + \left(\frac{\sigma_{SA}}{SA} \right)^2 + \left(\frac{\sigma_{dt}}{dt} \right)^2} \quad \text{Eqn D.2}$$

Where, σ_i is the error of each term, i. σ_{m_f} and σ_{m_i} are the standard deviations of each mass measurement and σ_{SA} is defined below in by the dimensions of the rectangle Eqn D.3 or tube Eqn D.4,

$$\sigma_{SA_{rect}} = 2 \sqrt{(W + T)^2 \sigma_L^2 + (L + T)^2 \sigma_W^2 + (W + L)^2 \sigma_T^2} \quad \text{Eqn D.3}$$

$$\sigma_{SA_{tube}} = \pi \sqrt{(OD + L)^2 \sigma_{OD}^2 + (L - ID)^2 \sigma_{ID}^2 + (OD + ID)^2 \sigma_L^2} \quad \text{Eqn D.4}$$

Where, W is the width, T is the thickness, L is the length, and OD and ID are the outer and inner diameters of CMC tubes. Noting that the errors in dimensional components are equal to 0.001 cm, σ_{SA} becomes close to zero.

D.2 Quantitative Rate Analysis

As several different reactions of SiC with either peroxide or its many possible reaction daughters are possible, the reaction rate of SiC above the core may be generally described by Eqn D.5

$$Rate_{above} = k_{H_2O} + k_{H_2O_2} [H_2O_2]^n_{above} \quad \text{Eqn D.5}$$

where, k_{H_2O} is the overall reaction rate constant (also the rate) in the presence of water at 300°C, $k_{H_2O_2}$ is the overall rate constant with respect to peroxide, $[H_2O_2]$ is the molar concentration of peroxide, and n is the net reaction order with respect to peroxide. k_{H_2O} will be the same for all three conditions. For this exercise, the average of all CVD samples in the out-of-core region, 1.36×10^{-9} mg/cm²s, was used (the single crystal sample was excluded due to the roughness difference with the polycrystalline samples). $k_{H_2O_2}$ was determined with the rate of the CVD samples (excluding the anomalous LR 1 sample), by re-arranging equation Eqn. 5.1. In the presence of radiation damage, both rate constants will change. Maeda et al [214] reported that

the electronic structure of SiC changes under ion irradiation, resulting in its increased corrosion susceptibility.

For the purposes of this analysis, the change in electronic structure can be assumed to correspond to a reduction in the activation barrier to corrosion. This assumption comes from use of transition state theory [152, 153, 213]. In this theory, the pre-exponential factor in the Arrhenius equation is interpreted to be dependent on physical constants, temperature, and an activation entropy. As that theory's assumptions are valid for corrosion systems, such as this, any radiation damage effect must be related to either the activation entropy or activation energy. As the activation entropy (ordering of the reacting system) is not likely to change due to point defect formation inside of SiC from radiation damage, radiation damage effects will appear in the activation energy.

If it is further assumed that the barrier reduction is identical both in respect to water and peroxide, the corrosion under irradiation can be described with the following equations Eqn D.6-Eqn D.8,

$$Rate_{above} = A_{H_2O} e^{-\frac{E_{a_{H_2O}}}{RT}} + A_{H_2O_2} e^{-\frac{E_{a_{H_2O_2}}}{RT}} [H_2O_2]_{above}^n \quad \text{Eqn D.6}$$

$$Rate_{rad} = A_{H_2O} e^{-\frac{E_{a_{H_2O}} + \Delta E_{rad}}{RT}} + A_{H_2O_2} e^{-\frac{E_{a_{H_2O_2}} + \Delta E_{rad}}{RT}} [H_2O_2]_{core}^n \quad \text{Eqn D.7}$$

$$Rate_{rad} = e^{-\frac{\Delta E}{RT}} (k_{H_2O} + k_{H_2O_2} [H_2O_2]_{core}^n) \quad \text{Eqn D.8}$$

where A_{H_2O} and $A_{H_2O_2}$ are the Arrhenius pre-exponential factors of the water and peroxide reactions with corresponding activation energies, $E_{a_{H_2O}}$ and $E_{a_{H_2O_2}}$, a change in the activation energy from radiation damage, ΔE , R is the universal gas constant, and T is the absolute reaction temperature.

For any given reaction order, n , with respect to peroxide, the rate constant with respect to peroxide can be estimated with a corresponding change in activation energy estimated from the in-core rate. As the average in-core rate is different for each sample type, this results in different activation energies and fractional increases, $e^{-\frac{\Delta E}{RT}}$, in the reaction rate constant, for each sample type. These are plotted for reaction orders up to 1 in Figure D.1

While this analysis method is not rigorous, several points are useful to draw from this graph. Possible reaction orders are given up to a reaction order of 1, after which the analysis indicates that radiation damage makes SiC more inert to corrosion. As that result is thoroughly inconsistent with previous work [91, 214, 215, 224], it is not considered. Applying this standard to LR SiC as well implies that the reaction order should be less than 0.5. This is significantly less than 1, implying that as H_2O_2 dissociates near/on a sample, its reaction products are mostly consumed before having an opportunity to react. OH, for example, has a half-life of about 10^{-7} seconds using the referenced model. Regarding the peroxide dissociation mechanism this would support the intermediate step of simple dissociation into OH radicals, which will be consumed quickly by the solution, while O_2 will be stable. .

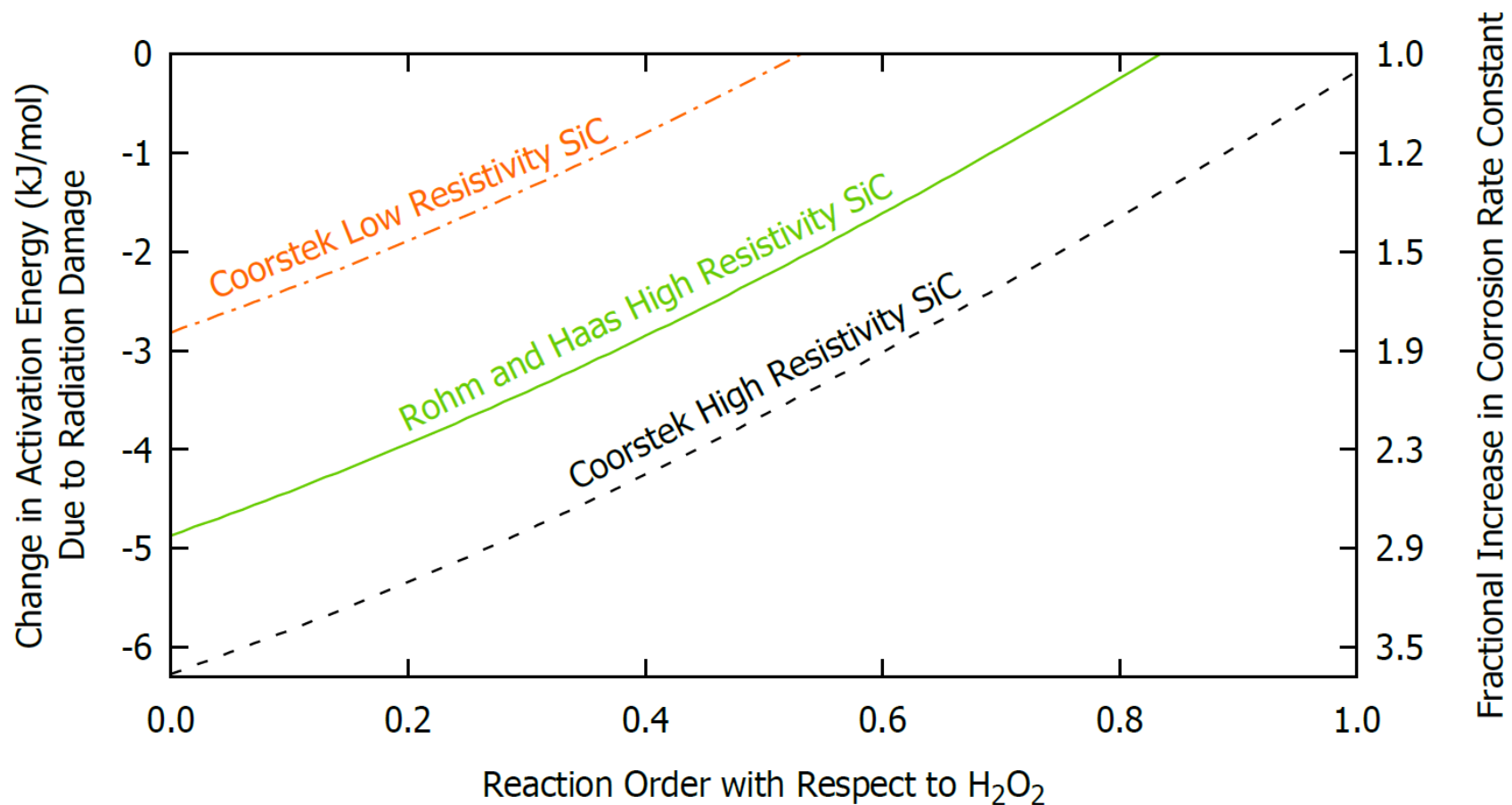


Figure D.1: Plot of the estimated change in corrosion activation energy (y-axis) and fractional increase in the rate constant from radiation damage (y2-axis) versus an assumed peroxide reaction order. Rates were determined from average values for above-core and out-of-core data, as well as sample-type-specific rates to give separate lines for each type, as labeled.

Further, regardless of the reaction order, there is a large and potentially significant difference between the LR and HR data sets; the corrosion activation energy for the HR samples is calculated to decrease by about twice that of the LR samples. In the event that LR SiC corrosion is not affected by radiation damage ($n = 0.5$), the HR samples still are affected by about a 4 kJ/mol activation energy barrier decrease. While this result is interesting, the combination of limited sample number, a single irradiation condition, and low signal-to-noise ratio in the data renders the above damage effects analysis uncertain. In particular, studies dedicated to H_2O_2 concentration and resistance effects are needed to evaluate this rigorously.

Vita

Peter Doyle was raised in Pittsburgh, PA, as one of four children. Being homeschooled through seventh grade, he began attending conventional schools in eighth grade, ultimately graduating from Carlynton Jr./Sr. High School in 2011. In August of 2011 he entered Geneva College as a Chemical Engineering and Chemistry student. After his Sophomore year, he attended the ACS and DOE sponsored Nuclear Chemistry Summer School in Brookhaven, NY, followed the next year by an internship at Westinghouse Electric Company. Following graduation in 2015, his graduate studies began in August 2015 at the University of Tennessee. In 2017 he obtained a Master's Degree in Nuclear Engineering after defense of a thesis on "Modeling of Dislocation Channel Formation and Evolution in Irradiated Metals". His professional interests include aqueous corrosion, especially as related to nuclear power plants, fundamental materials science in radiation effects, scientific computing, and chemical characterization techniques.