

Final Report for Project:

Development of Self-Healing Zirconium-Silicide Coatings for Improved Performance Zirconium-Alloy Fuel Cladding

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Executive Summary

Zirconium-alloy fuel claddings have been used successfully in Light Water Reactors (LWR) for over four decades. However, under high temperature accident conditions, zirconium-alloys fuel claddings exhibit profuse exothermic oxidation accompanied by release of hydrogen gas due to the reaction with water/steam. Additionally, the ZrO_2 layer can undergo monoclinic to tetragonal to cubic phase transformations at high temperatures which can induce stresses and cracking. These events were unfortunately borne out in the Fukushima-Daiichi accident in Japan in 2011. In reaction to such accident, protective oxidation-resistant coatings for zirconium-alloy fuel claddings has been extensively investigated to enhance safety margins in accidents as well as fuel performance under normal operation conditions. Such surface modification could also beneficially affect fuel rod heat transfer characteristics. Zirconium-silicide, a candidate coating material, is particularly attractive because zirconium-silicide coating is expected to bond strongly to zirconium-alloy substrate. Intermetallic compound phases of zirconium-silicide have high melting points and oxidation of zirconium silicide produces highly corrosion resistant glassy zircon (ZrSiO_4) and silica (SiO_2) which possessing self-healing qualities.

Given the long-term goal of developing such coatings for use with nuclear reactor fuel cladding, this work describes results of oxidation and corrosion behavior of bulk zirconium-silicide and fabrication of zirconium-silicide coatings on zirconium-alloy test flats, tube configurations, and SiC test flats. In addition, boiling heat transfer of these modified surfaces (including ZrSi_2 coating) during clad quenching experiments is discussed in detail.

Oxidation of bulk ZrSi_2 was found to be negligible compared to Zircaloy-4 (a common Zr-alloy cladding material) and mechanical integrity of ZrSi_2 was superior to that of bulk Zr_2Si at high temperatures in ambient air. Very interesting and unique multi-nanolayered composite of ZrO_2 and SiO_2 were observed, which is unlike other commonly observed in oxidation of transition metal silicides such as MoSi_2 . A physical model for the oxidation has been proposed wherein Zr–Si–O mixture undergoes a spinodal phase decomposition into ZrO_2 and SiO_2 , which is manifested as a nanoscale assembly of alternating layer of the two oxides. Steam corrosion at high pressure (10.3 MPa) led to weight loss of ZrSi_2 and produced oxide scale with depletion of silicon, possibly attributed to volatile silicon hydroxide, gaseous silicon monoxide, and a solubility of silicon dioxide in water. Only Zircon phase (ZrSiO_4) formed during oxidation of ZrSi_2 at 1400 °C in air, and allowed for immobilization silicon species in oxide scale in the aqueous environments.

Zirconium-silicide coatings (on zirconium-alloy substrates) investigated in this study were deposited primarily using magnetron sputter deposition method and slurry method, although powder spray deposition processes cold spray and thermal spray methods were also investigated. The optimized ZrSi_2 sputtered coating exhibited a highly protective nature at elevated temperatures (700 °C, 1000 °C, and 1200 °C) in ambient air by mitigating oxygen permeation to the underlying zirconium alloy substrate. The high oxidation resistance of the coating has been shown to be due to nanocrystalline SiO_2 and ZrSiO_4 phases in the amorphous oxide film matrix which develops at high temperatures. The coating prevented oxide formation in Zircaloy-4 substrate in high-pressure steam condition even if the top surface of the coating was degraded by formation of zirconium-rich oxide layer. Cold spray and thermal spray deposition of ZrSi_2 have been performed by systematically varying deposition parameters. While deposition of coating was achieved, further process optimization is required to improve coating quality deposited using these methods. An optimal zirconium-silicide slurry coating for mechanical properties and corrosion resistance/oxide protection was developed based on a theoretical characterization. The slurry coating was investigated using a range of similar compositional coatings to accurately characterize the best coating with respect its mechanical integrity and environmental protection for zirconium alloy substrates. It was determined that the fine grained composite coatings could provide excellent mechanical advantages and oxidation protection to zirconium alloy but is limited due critical oxide scale growth on the underlying substrate. It

was also confirmed that the theoretical composition coating enhanced oxidation protection and wear resistance.

Distinctive oxide layers of ZrSi_2 prepared at 1000 °C and 1400 °C in ambient air were subjected to a 3.9 MeV Si^{2+} ions irradiation at 305 °C and their radiation responses were characterized and analyzed. Nanocomposite oxides consisting of ZrO_2 nanocrystals embedded in amorphous SiO_2 matrix formed on ZrSi_2 surface after oxidation at 1000 °C. Radiation-induced phase mixing of the oxide phases and amorphization of ZrO_2 was observed up to ~ 820 nm in depth, about one-third of the total radiation damaged region (2.5 μm in thickness) as estimated by SRIM calculation. The ion-mixing was facilitated with fine ZrO_2 grains (< 25 nm) at low doses (5 to 10 dpa) but not in larger grains (> 30 nm) even at high damage levels (30 to 60 dpa). Qualitative explanation of the ion-mixing of the nanocomposite was proposed with respect to grain size of ZrO_2 in SiO_2 matrix. Polygonal crystalline ZrSiO_4 grains in dual-layered oxide scale on ZrSi_2 at 1400 °C were completely amorphized under the ion-irradiation. Given the high corrosion resistance of ZrSiO_4 and immobilization of Si in aqueous environments conclusively demonstrated in this study), it is anticipated that the irradiated oxide scale would have a superior corrosion resistance compared to unirradiated surface. The structurally and compositionally homogenous microstructure resulting from radiation damage would eliminate preferential corrosion sites such as grain boundaries and local Si rich region on the surfaces. However, further experimental work will be required to confirm the radiation-enhanced corrosion resistance. The results can be applied to not only baseline data for radiation response of the potential neutron deflector in advanced reactors but also development of nanocomposite structural materials in future spacecraft, sensors, detector subjected to high radiation dose.

A quench test facility was designed and built to study boiling and quenching behavior of zirconium-silicide coated surfaces at various system conditions (e.g., elevated pressures and water subcooling). The efficacy of this test facility has been demonstrated using bare Zircaloy-4 rodlets. The experiments consisted of pressurized tests (pressure range of 0.1 MPa to 0.6 MPa in saturated water) and subcooling tests (atmospheric pressure in 0 K to 40 K subcooled water). The minimum film boiling temperature for bare Zircaloy-4 increased with increasing system pressure and water subcooling consistent with past literature data. Quenching heat transfer was improved by the surface coating; the minimum film boiling temperatures were increased in the range of 6 to 8 % in these conditions possibly due to a small thermal conductivity of the ZrSi_2 coating. While these improvement factors are quite low, the study points to the potential use of coatings to beneficially affect heat transfer of the cladding. Even after three aggressive thermal cycles (e.g., water quenching from 700 °C to 85 °C in 20 seconds), the coating did not exhibit any surface degradation such as cracking or spallation.

The project provided a fertile ground for training the next generation of students in the area of nuclear reactor materials, including materials processing, testing, and characterization. At least seven students and two post-doctoral scientists from the nuclear engineering and materials science and engineering disciplines participated and were supported by this project. Four journal articles and four conference proceedings have thus far accrued from this project and two additional journal articles are presently under preparation. Additionally, the findings of this research were presented in six national conferences. Details of these publications and presentations are provided at the end of the report. A graduate student working on this project received the Graduate Excellence in Materials Science (GEMS) award from the American Ceramic Society in 2016. The project also provided a platform for the establishing a DOE International Nuclear Engineering Research Initiative (INERI) collaboration with POSTECH university in Pohang, S. Korea. Although not funded on the US side, the INERI facilitated a very dynamic scientific collaboration between the students and faculty at the University of Wisconsin and POSTECH.

We thank the U.S. Department of Energy – NEUP program for providing funding for this project.

Chapter 1: Introduction

1.1. Accident Tolerant Fuel

Zirconium-alloy (Zr-alloy) fuel claddings have been widely used in light water nuclear reactors (LWR), for over four decades due to their excellent neutron transparency and combination of corrosion resistance and mechanical properties in normal operating conditions [1]. Boiling water reactors (BWR) currently use Zircaloy-2 (Zirc-2) but cladding of pressurized water reactors (PWR) has transitioned from Zircaloy-4 (Zirc-4) to zirconium-niobium claddings (i.e., M5 and ZIRLO) due to its improved corrosion resistance behavior [2].

Table 1.1. Composition of the Zirconium alloy (weight percent, Zr balanced) [3]

Alloy	Nb	Sn	Fe	Cr	O
Zirc-2	-	1.4	0.1	0.1	0.12
Zirc-4	-	1.5	0.2	0.1	0.14
M5	1	-	0.05	0.02	0.14
Zirlo	1	1	0.1	<0.01	0.11

Since the Fukushima accident in 2011, the behavior of the UO_2 -zirconium alloy fuel system under the severe accident conditions has been an issue. As a result, interest on advanced fuels for LWR has shifted from improving fuel performance under normal operating conditions to maximizing safety margins under design-basis and beyond-design-basis accident scenarios. One accident scenario is the degradation of the reactor core by the coolant-limited condition, where the primary cooling system does malfunctions as was the case in the Fukushima accident. Therefore, removing decay heat from fuel rods to a level of about 5 to 6% of full power immediate after scram [4], is a critical issue. An accident is progressed when cooling capability is lost via pipe leakage or pump failure. During the lead-up phase, the fuel cladding temperature increases due to decay heat and the remaining coolant starts to boil. As the fuel reaches about 800 °C, chemical and physical degradation of zirconium alloy cladding becomes significant. If pressure inside the reactor vessel is low and the emergency core cooling system (ECCS) is active at this point, additional coolant is ejected into the core and the fuels could be quenched and cooled down. Otherwise, a large amount of zirconium alloy claddings in the core would react with high temperature steam, leading to loss of intrinsic mechanical properties of the fuel cladding because of oxide layer formation and hydrogen embrittlement, also referred to as hydriding [5–7]. This fuel cladding degradation would induce fuel failure and a release of radioactive materials into the reactor vessel. Since the oxidation of Zr-alloy is highly exothermic, the core temperature continues to increase to about 1500 °C when extensive fuel cladding failure occurs. In this phase, management and retention of radioactive material inside reactor containment is important while avoiding hydrogen combustion (hydrogen is a byproduct of the Zr-alloy oxidation in steam).

In response to accident scenarios, the concept of innovative approaches in the development of advanced technology fuels (ATF) was introduced by the Department of Energy in the aftermath of the Fukushima accident. The ATF program is aimed at developing fuels that can tolerate higher temperatures that can a result of the loss of active cooling, for a longer time than conventional UO_2 -zirconium alloy fuel system [2] to increase coping time in response the accident. The technical requirement for ATF is addressed in the DOE report [8] as shown in Figure 1.1. First, ATF cladding is required to have slower reaction kinetics in high temperature steam, minimizing hydrogen generation compared to the current Zr alloy claddings. It is necessary to maintain the cladding's mechanical stability in excess of 1200 °C and thermal shock (due to activation of ECCS) in order to prevent a large release of fission products. Moreover, enhanced heat removal from the fuel would be beneficial to mitigating further core degradation. Second, it is recommended that the ATF fuel pellet has improved thermal/mechanical properties such as higher density, higher thermal conductivity, and higher melting point to make accident progress slower. It also minimizes

both the fuel cladding chemical interactions (FCCI) and fuel cladding mechanical interactions (FCMI) and has structurally to improve retention of fission products. Last, ATF has to maintain its good performance under normal operation conditions and must be compliant with current core design, reactor operation, as well as the economic and safety requirements.

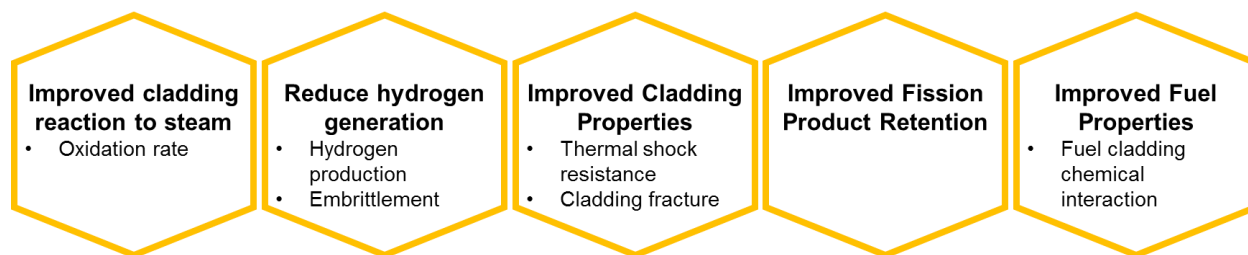


Figure 1.1. Design objective of ATF system addressed in DOE report to U.S. Congress.

There have been three major approaches to enhance the safety margin of LWR fuels: development of alternative fuel rod cladding materials as complete replacement for Zr-alloy, a fabrication of thin protective coatings on Zr alloy cladding surface, and investigation of alternative fuel forms. Some examples of replacements for Zr-alloy include FeCrAl alloys [9,10], SiC-SiC composites [7,11], and molybdenum cladding [12]. For oxidation resistant coatings, chromium [13,14], Ti_2AlC [15], and TiN [16] thin coatings deposited on the Zr-alloy cladding are being investigated to take advantage of their protective behavior. Uranium-silicide and uranium-nitride are being explored as alternative fuel forms [17].

The main goal of this study is to develop novel corrosion resistant thin coatings on the Zr-alloy surface, minimizing modification of the existing fuel system; e.g., using zirconium silicide (Zr-Si) coating material. In this work, Zr-silicide surface coatings are prepared using various techniques; i.e., magnetron sputter deposition (PVD), cold spray (CS), thermal spray (TS), and slurry method (SL). Performance of the modified surfaces has been evaluated in terms of oxidation and heat transfer using high temperature air tests, high temperature water tests, and heat transfer quench tests followed by metallurgical characterization methods. Finally, ion-irradiation response of oxidized Zr-Si materials was investigated by electron microscopes. Detailed extension of this work will be the focus of the proposed research program.

1.2. Zirconium Silicide

Transition-metal silicides have been widely used in many fields (e.g., aerospace, microelectronics, and medical) due to its superior oxidation resistance, a low electrical resistance, a low density, and excellent mechanical properties at high temperatures [18–23]. Among silicides, zirconium-silicides are expected to be a promising material in nuclear industry as a neutron reflector [23] or accident tolerant coatings for fuel cladding in LWR. The materials have a good high temperature stability as seen in Zr-Si binary phase diagram (Figure 1.2). Intermetallic of Zr-Si phases has a high melting point. For examples, Zr_2Si , ZrSi, and $ZrSi_2$ are stable up to 1927 °C, 2203 °C, and 1626 °C, respectively.

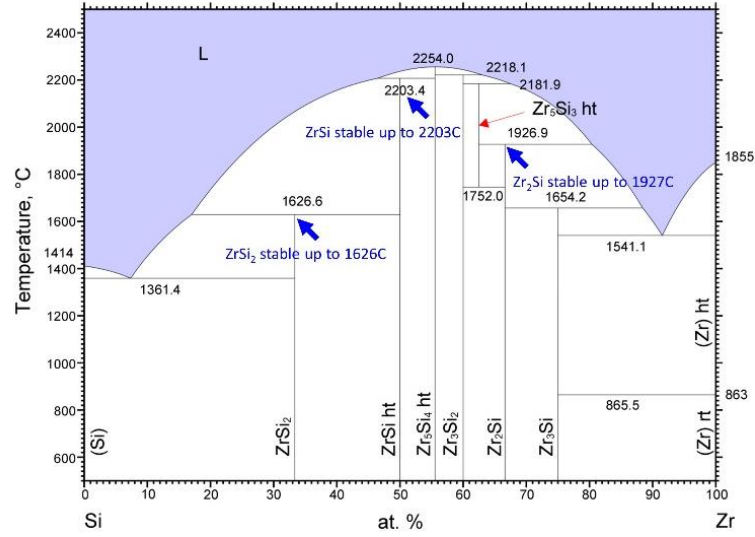


Figure 1.2. Zr-Si binary phase diagram [24].

Silicon-rich zirconium silicide stoichiometries, ZrSi_2 , has an orthorhombic base-centered lattice structure (C49) and the conventional unit cell has a total of 12 atoms (see Figure 1.3). Based on theoretical calculations and experiments, the lattice parameters and atomic arrangement are summarized in Table 1.2. It is generally known that a ratio of distortion (b/a) is large compared to other metal silicides having similar structures (e.g., NbSi_2 , TiSi_2 , MoSi_2), leading to anisotropic mechanical and electrical properties. In addition, physical and mechanical properties of ZrSi_2 were reported as follows: a high hardness ($> 850\text{HV}$), a low density (4.89 g/cm^3), high creep deformation at high temperatures [19], high Young's modulus ($230\text{ GPa} - 268\text{ GPa}$ at room temperature) [21], and a large yield stress at elevated temperatures ($70\text{ MPa} - 175\text{ MPa}$ at $1000\text{ }^\circ\text{C}$) [20]. A linear thermal expansion coefficient of ZrSi_2 is on the same order as zirconium alloy [19,25] so that significant shear stress evolution at the interface between ZrSi_2 coating and zirconium alloy cladding at elevated temperature would not be expected; a linear thermal expansion coefficient of ZrSi_2 at $200\text{ }^\circ\text{C}$ was determined to be $8.5 \cdot 10^{-6}\text{ K}^{-1}$ and that of zirconium alloy at $100\text{ }^\circ\text{C}$ was in the range of $5.5 \cdot 10^{-6}\text{ K}^{-1}$ to $11 \cdot 10^{-6}\text{ K}^{-1}$. Finally, its resistance to oxidation via formation of a tenacious oxide layer (ZrO_2 and SiO_2) is highly probable.

Table 1.2. The lattice constants ($\text{\AA}$) of orthorhombic ZrSi_2 .

	a_0	b_0	c_0
Rosenkranz et al. (1992) [19]	3.721	14.68	3.683
Nakano et al. (2003) [20]	3.72	14.68	3.72
Hao et al. (2015) [22]	3.706	14.735	3.672

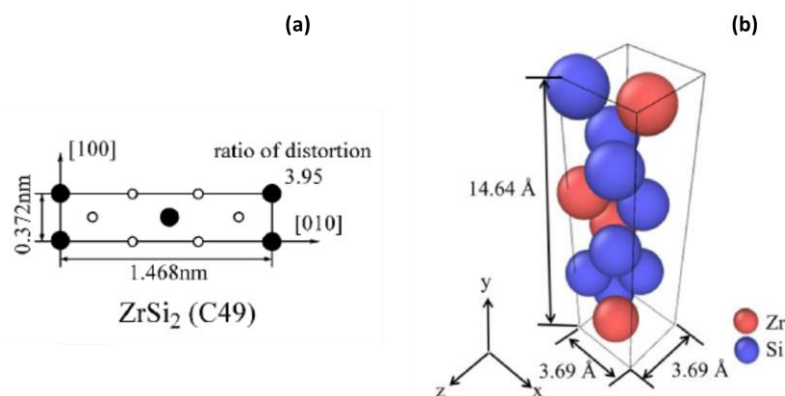


Figure 1.3. (a) Atomic arrangements on (001) atomic plane [20], and (b) a conventional unit cell of ZrSi_2 [21].

1.3. Coating Technologies

Methods for deposition of coatings and surface modification of materials as attempts to improve corrosion/oxidation resistance of structural materials has been extensively investigated. In general, deposition processes is categorized into the four techniques as follows [26]:

- Gaseous state process: Chemical vapor deposition (CVD), physical vapor deposition (PVD), and ion beam assisted deposition (IBAD)
- Solution state process: Chemical solution deposition, electrochemical deposition, and sol-gel and slurry method (SL) deposition
- Molten or semi-molten state process: Thermal spraying deposition (TS) and welding
- Solid state process: Cold spraying deposition (CS)

Since each deposition technique has distinct characteristics such as deposition rate, deposition temperature, and limitations of substrate and coating material, many studies have been performed to enhance oxidation resistance of materials by applying protective surface coatings. Examples are thin TiN film deposited on stainless steel bars by a pulsed laser deposition method [27], molybdenum-disilicide coating using high velocity oxyfuel process on carbon steel substrate [28], and chromium coating by reactive radio frequency magnetron sputtering on low carbon steel [29], and the coatings showed a certain level of success.

Magnetron sputter deposition is one of the physical vapor deposition (PVD) methods. As seen in Figure 1.4, glow discharge plasma is formed in front of a cathode by high electric potential at very low pressure. Energetic ions generated (generally Ar^+) in the glow discharge plasma bombard a target and sputtered target atoms, then condense on a substrate and form a thin film. To improve the low deposition rate and substrate heating effects, magnetron sputtering has been developed and uses a magnetic field to constrain secondary electron motion near the target. Increasing probability of Ar ion generation, in turn, leads to higher deposition rates of the thin film [30]. The main benefits for the PVD coating are summarized as follows [26]: Surface cleaning via plasma prior to deposition, a high purity of coating, uniform coating thickness, flexibility over a wide range of coating and substrate materials, and controllable coating structure varying deposition parameters. Thornton postulated that a coating morphology is a function of argon pressure and substrate temperature (see Figure 1.5) [31]. At higher substrate temperatures, sputtered atoms have high surface and bulk diffusivity so that the dense columnar or equiaxed grains would be formed (Zone 2 and Zone 3). At high argon gas pressure, increasing collision between argon atoms and sputtered atoms leads to a shifting boundary of Zone 1 to high temperatures.

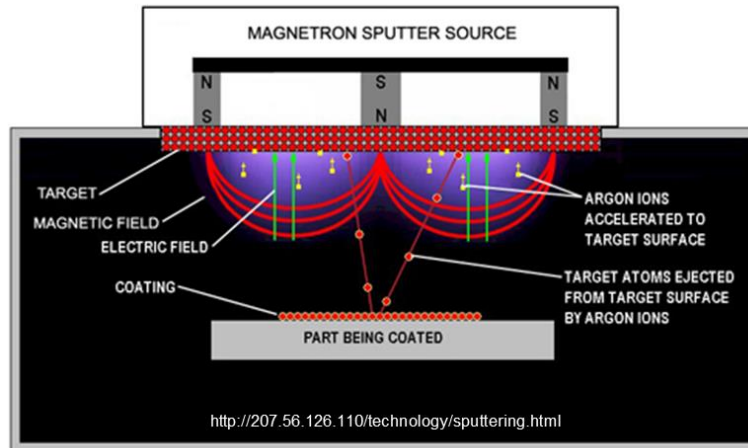


Figure 1.4. Schematic illustration of magnetron plasma vapor deposition process.

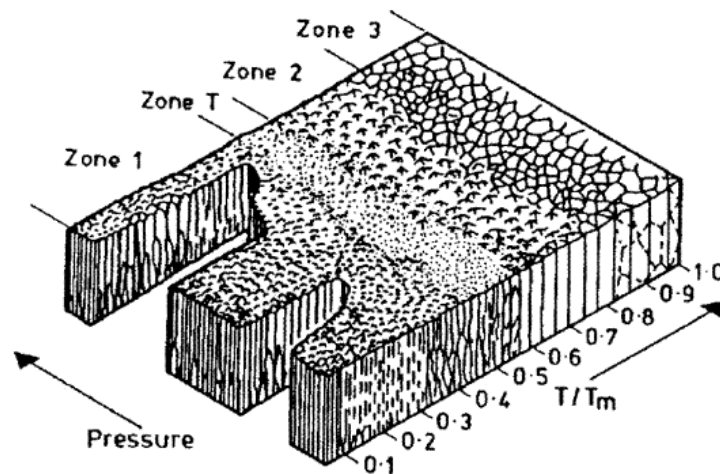


Figure 1.5. Schematic representation of microstructure of coatings by magnetron sputtering using argon ions. T is substrate temperature and T_m is a melting point of the coating material [31].

Cold spray method is a solid-state deposition processes for fabricating a coating by propelling micron size particles with a supersonic velocity to a substrate. The conventional cold spray system is illustrated in Figure 1.6. The particles are accelerated by a high pressure gas and undergo adiabatic shear deformation during the impact on the substrate, resulting in adhesion to the surface and subsequently cohesion between particles [32]. Depending on gas pressure and cold spray nozzle system, velocity of the particle is in the range of 300 to 1400 m/s and the powder particle must exceed a certain critical impact velocity to achieve adhesion, but it should be below a certain velocity to minimize erosion [33]. The main advantage of cold spray deposition is as follows: a high efficiency of deposition, avoidance of undesirable phases or oxide formation, and a short deposition time.

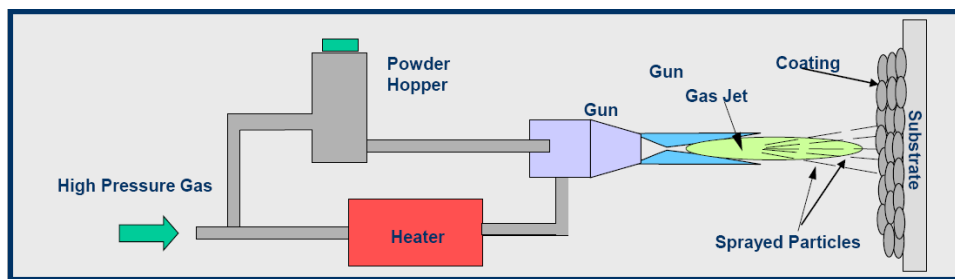


Figure 1.6. Schematic illustration of cold spray system [34].

Thermal spray process uses concentrated heat source to melt powder feed-stock and then propels the molten droplets on to the surface of a substrate or the part to be coated [35]. The molten particles form a ‘splat’ on the substrate surface, spread out, and cool rapidly to form a coating. Plasma spray process, one of thermal spray techniques, provides for high plume temperatures, higher particle kinetic energy, and higher coating density and phase purity. Since melting process of feedstock powders is important parameter in thermal spray technique, a distance between a spraying nozzle and a target substrate can be adjusted during the spraying. In addition, effect of surface preparation such as a grit blasting to evaluate its role on interface bonding strength.

Polymer-derived ceramic coating process (e.g. slurry coating) is a practical method to coat complex geometries with preceramic polymers. Subsequent heat treatment results in formation of a thin layer of Si-based, Al-, B- or Ti-based ceramics. Cracks can be formed during pyrolysis due to shrinkage of the preceramic polymer but adding active/inert filler (fine particles) in the polymer can mitigate the defect formation. Typical polymer precursors are stable at room temperature and due to their viscous natures (when in a liquid phase) or hard solid structure (such as some cage structured polysilsequioxanes) to implement proper and effective fabrication methods many of the polymers must be altered [36]. Fortunately, simple methods involving organic solvents can be implemented for most precursors to easily adjust for rheological behavior such as viscosity and allow for complex shaping and forming during fabrication using conventional composite fabrication technology. The greatest advantage that slurry coatings have over conventional CVD, PVD, and sol-gel methods (via hot pressing or sintering) is that the processing temperatures for high purity ceramics are relatively low with pyrolysis occurring at temperatures as low as 400 °C. This is significant in limiting ceramic degradation and is vital for widening the use of ceramics as possible coatings for metal substrates since metals can undergo significant structural changes at higher temperatures.

Chapter 2: Oxidation of Bulk Zr-Si Compounds

Understanding oxidation and corrosion behavior of bulk zirconium silicide materials (e.g., ZrSi_2 , Zr_2Si) is must precede the evaluation feasibility of zirconium silicide coatings as a protective barrier for Zr-alloy. To this end, air oxidation of bulk ZrSi_2 and Zr_2Si in ambient air and steam corrosion tests of bulk ZrSi_2 were performed and characterized in detail.

2.1. High Temperature Air Oxidation

The oxidation behavior of dense bulk forms of ZrSi_2 in high temperature air (700 °C, 1000 °C, 1200 °C, and 1400 °C) was investigated. A temperature of 700 °C was chosen to determine if the material degrades at low temperature, while higher temperature tests (1000 °C, 1200 °C, and 1400 °C) were performed to simulate a postulated loss of coolant accident (LOCA) scenario in light water reactors. To demonstrate compositional effects on oxidation behavior, bulk Zr_2Si was oxidized at 1200 °C in ambient air. In addition, Zircaloy-4 (Zirc-4) was also oxidized under similar conditions as a base-line for comparison with ZrSi_2 . All oxidized samples were rigorously characterized with the goal of understanding compositional and morphological evolution of micro- and nano- oxide structures at the materials' surface.

2.1.1. Oxidation Kinetics and Oxidation Products of ZrSi_2

The kinetics of oxidation of the dense bulk ZrSi_2 was determined by weight change measurements at each hour during oxidation. The weight gain values (per unit area of the sample) of Zirc-4 and dense ZrSi_2 at 700 °C, 1000 °C, and 1200 °C are shown in Figure 2.1. As may be noted, the weight gain of the dense ZrSi_2 is negligible compared to that of the Zirc-4 at the high temperatures. Zirc-4 showed the formation of a thick oxide scale and its spallation led to weight reduction at 1000 °C (4 hours) and 1200 °C (3 hours) as shown in Figure 2.1a. On the other hand, the bulk ZrSi_2 appeared to be stable without significant degradation at the high temperatures. It is worth noting that no pest oxidation was observed on the surface of the ZrSi_2 samples, as has been observed for example in oxidation of MoSi_2 for other applications [37]. Minor chipping on the edge of the bulk ZrSi_2 samples was observed at 1200 °C after 3-hour oxidation. Therefore, the weight gain values at 5 hours have not been reported in Figure 2.1b. The general oxidation kinetics followed a power law, with oxidation kinetics at 700 °C and 1000 °C following approximately a parabolic rate kinetics while at 1200 °C the oxide layer growth obeyed more closely the cubic growth rate law. More protective nature with increasing temperatures have been reported in MoSi_2 and TiSi_2 as well, resulting from denser SiO_2 formation [37–39]. The weight gain relationships are empirical and were plotted with the limited data points so that it is difficult to elucidate physical and chemical processes of the oxide growth. Nevertheless, the weight gain trends imply the kinetics of oxidation of ZrSi_2 as a material is controlled by the diffusion of charged species (e.g., Si^{4+} , O^{2-}) through the growing oxide layer.

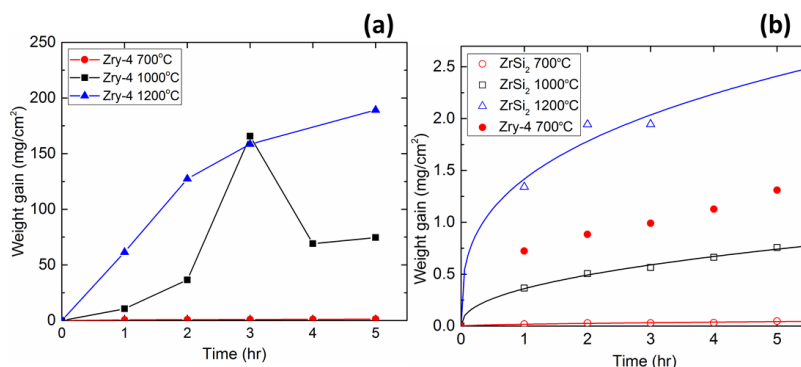


Figure 2.1. Weight gain vs. exposure time for (a) Zirc-4 and (b) bulk ZrSi_2 samples constructed with least square fits at 700 °C, 1000 °C, and 1200 °C in ambient air.

The oxide layer thickness was measured in SEM cross-sectional images and shown in the Figure 2.2. The average oxide layer thickness of the dense ZrSi_2 at 700 °C, 1000 °C, 1200 °C, 1400 °C for 5-hour oxidation was determined to 470 nm, 6.7 μm , 37 μm , and 31 μm , respectively. In addition, the oxide layer thickness at 1000 °C for 15-hour oxidation was 12 μm , which considered together with other exposure times at this temperature is indicative of parabolic oxidation kinetics at 1000 °C. An important observation was that the average thickness of oxide layer at 1400 °C was thinner than that at 1200 °C even though both oxidation tests were performed for 5 hours in ambient air environment. In general, oxidation process is strongly accelerated at higher temperature conditions. The thinner oxide scale in 1400 °C has been attributed to the formation of a highly corrosion resistant zircon layer (ZrSiO_4) at this high temperature. Furthermore, no spallation and delamination of the oxide layer were observed and only minor cracks were identified in unreacted ZrSi_2 matrix underneath the oxide scale at 1200 °C possibly due to thermal cycling due to periodic removal of samples from the furnace.

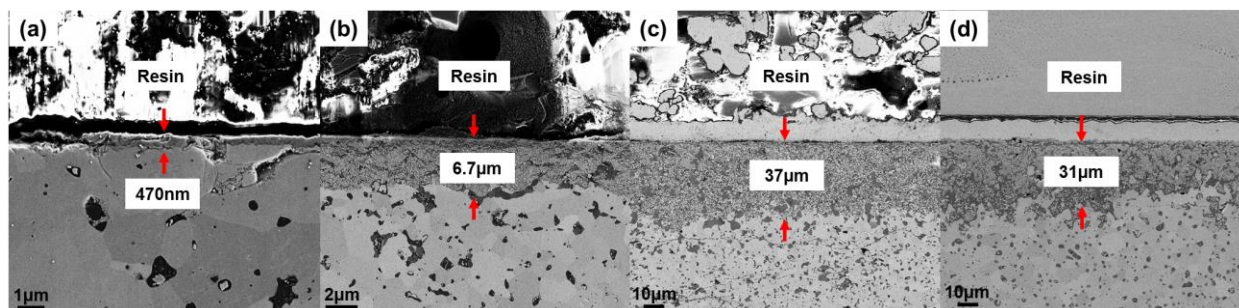


Figure 2.2. Cross-sectional SEM images of the dense ZrSi_2 at (a) 700 °C, (b) 1000 °C, (c) 1200 °C, and (d) 1400 °C for 5-hour exposure in air. The red arrows indicate the oxide layer between a mounting resin and unreacted ZrSi_2 .

Although thickness of the ZrSi_2 oxide layer formed at high temperatures is significantly lower than that formed on Zirc-4, the oxide scale is much thicker than for TaSi_2 , MoSi_2 , and WSi_2 in the similar oxidation tests (1000 °C air) reported in literature [40]. One of possible reason for this is the thermodynamically favored ZrO_2 formation in ZrSi_2 oxidation. Figure 2.3 shows Gibbs free energy of formation of oxide per a mole of O_2 of Si as compared to those of Ta, Ti, Mo, W, and Zr, which was calculated by HSC Chemistry thermodynamics software. In these other metal-silicides except for Ti, selective oxidation of Si leads to formation of a continuous oxidation resistant SiO_2 layer while the absence of continuous SiO_2 layer in ZrSi_2 may result in relatively faster oxide growth [41]. Likewise, TiSi_2 has at least five times higher oxidation rate compared to MoSi_2 [39].

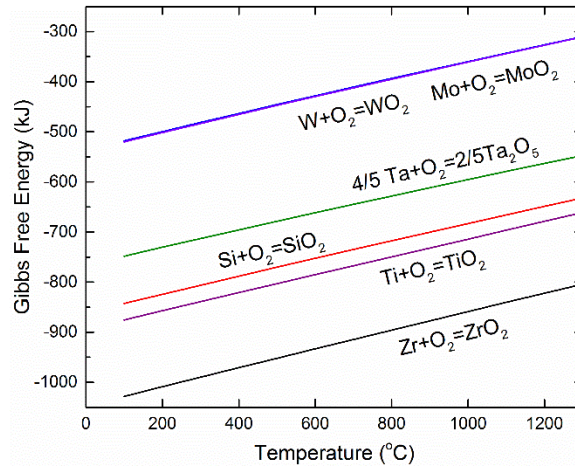


Figure 2.3. Gibbs free energies of oxide formation for Zr, Ti, Si, Ta, W, and Mo per 1 mole O_2 , calculated by HSC Chemistry thermodynamics software.

The phases present in the oxide layer formed at different temperatures for 5-hour exposure were identified by full-theta x-ray diffraction analysis and the results are shown in Figure 2.4. At 700 °C oxidation, pronounced diffracted peaks stemming from unreacted $ZrSi_2$ and weak Si and monoclinic ZrO_2 (m- ZrO_2) peaks were also identified. At 1000 °C and 1200 °C oxidation, intensity of m- ZrO_2 remarkably increased and weak Si peaks were also seen. Grazing incidence XRD scan (2 ° incident beam angle) showed the same results. For higher temperatures, the intensity of the strongest m- ZrO_2 peak at 28 ° (111) gets sharper but the strongest peak of $ZrSi_2$ at 39 ° (131) gets weaker and broader, which corresponds to thicker ZrO_2 oxide layer at higher temperature. In addition, absence of peaks of thermodynamically favored SiO_2 and zircon ($ZrSiO_4$) phases observed in Zr-Si-O system does not preclude their presence, since they may be present as amorphous phases. During the selective oxidation of Zr in $ZrSi_2$, some Si may be newly formed as an intermediate product which represents the weak silicon peak at 47° (220). Geßwein et al. postulated selective oxidation producing SiO_2 and Si at low temperature (as shown in equation 2.1) from thermogravimetric experiments of $ZrSi_2$ powders oxidation in air [42].

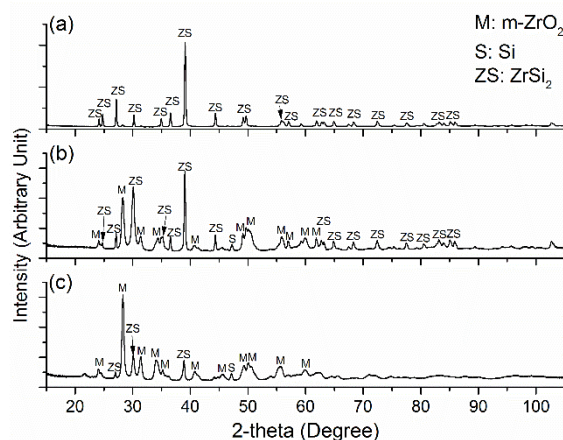
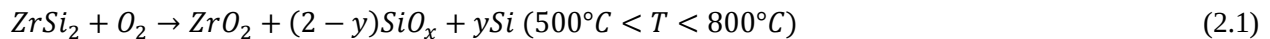


Figure 2.4. XRD patterns of the $ZrSi_2$ oxidized at (a) 700 °C, (b) 1000 °C, and (c) 1200 °C for 5 hours showing monoclinic zirconia, silicon, and $ZrSi_2$ peaks.

To test the hypothesis that formation of zircon is a kinetically limited process even if formation is thermodynamically favored, long-term oxidation tests of ZrSi_2 at 1200 °C for 50-hours was performed. The oxidized ZrSi_2 showed spallation of the oxide layer during the cooled down period. X-ray diffraction analysis of the oxidized ZrSi_2 sample (Figure 2.5) revealed strong peaks of zircon and weak peaks for ZrO_2 and SiO_2 . This result supports the hypothesis that the formation of zircon is kinetically limited.

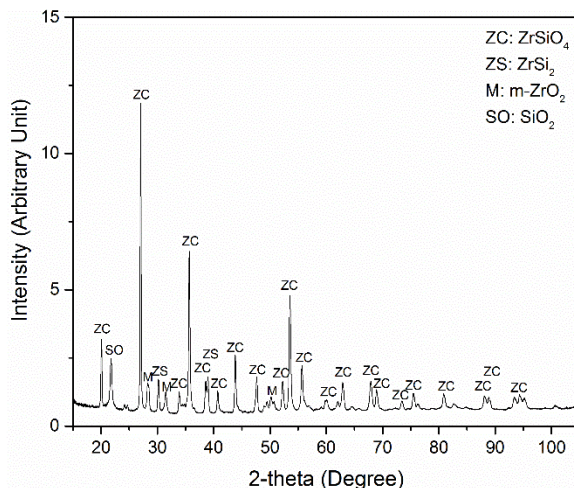


Figure 2.5. XRD pattern of oxidized ZrSi_2 at 1200 °C for 50 hours in ambient air, revealing crystalline ZrSiO_4 (zircon) phase.

2.1.2. Evolution of Oxide Surface Morphology in ZrSi_2

To investigate the compositional and morphological evolution of the oxide layer at high temperatures, plan-view SEM-EDS examinations were first performed for samples exposed to each of the temperatures. Figure 2.6a shows SEM image of the surface of the as-received ZrSi_2 and Figure 2.6b shows surface of ZrSi_2 sample that was subject to oxidation at 700 °C for 5 hours. Figure 2.6c and Figure 2.6d show results of EDS analysis of the oxide layer. Micron-sized spherical phases were observed to evolve on the oxidized surface (Figure 2.6b). Semi-quantitative EDS point scan confirmed that there were local variations in the concentration of Si, Zr, and O on the surface and the spherical phases were enriched in Si (i.e., point 1 and 2 in Figure 2.6c). This represents a significantly higher Si concentration than in the as-received ZrSi_2 for which the Zr-to-Si ratio was 1:2.4 as determined by our XPS, to be discussed later. Therefore, the micron-scale spherical phases appear to be Si-rich oxides formed by Si diffusion from the surrounding area.

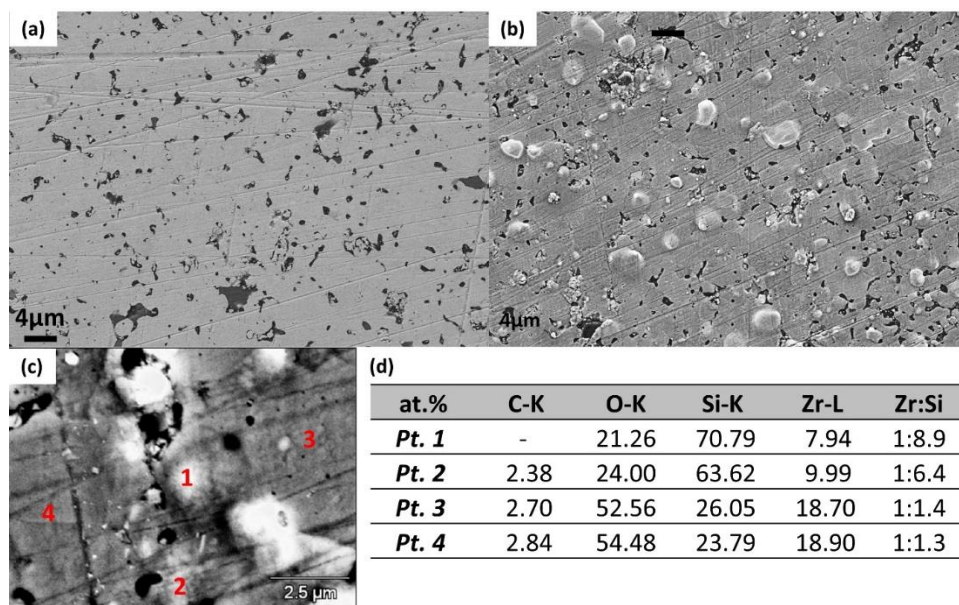


Figure 2.6. Plan-view of SEM images of (a) as-received ZrSi_2 , (b) ZrSi_2 oxidized at 700 °C for 5 hours, (c) high voltage SEM (12 kV) image of the oxidized sample, and (d) EDS compositions in regions indicated in (c). Points 1 and 2 indicate the regions of spherical phases shown in the image (b).

On surfaces of samples oxidized at higher temperatures, the surface morphology was different as shown in Figure 2.7 for samples oxidized at 1000 °C, 1200 °C, and 1400 °C. The Si rich humps were not clearly observed but new surface features started revealing. At 1000 °C, fine oxide phase particles also emerged on the surface but the size of structure was too small to be quantified by SEM imaging. The nano-scale precipitation of oxide phase particulates (40nm to 100nm in size) appeared particularly on the surface of samples oxidized at 1200 °C for 5 hours (Figure 2.7b). The imaging contrast between the background matrix and oxide particulates suggests differences in their compositions and TEM-EDS analysis determined that these nano-sized particulates were ZrO_2 as will be discussed later. The surface morphology of the long-term oxidized ZrSi_2 (Figure 2.7c) showed distinct features 100-200 nm in size of zircon phase in SiO_2 matrix. It is speculated that the nano-scale spherical ZrO_2 phases was formed in SiO_2 matrix in the early stages of ZrSi_2 oxidation and then reacted with each other to form zircon phase and coalesce as oxidation progressed. Finally, fully developed zircon phases were observed at the oxidized surface at 1400 °C for 5 hours (Figure 2.7d) with grains which were 10 to 20 times larger than those formed on the surface on oxidized ZrSi_2 at 1200 °C for 50 hours. The result indicates that oxidation temperature is a more dominant factor than duration of oxidation process.

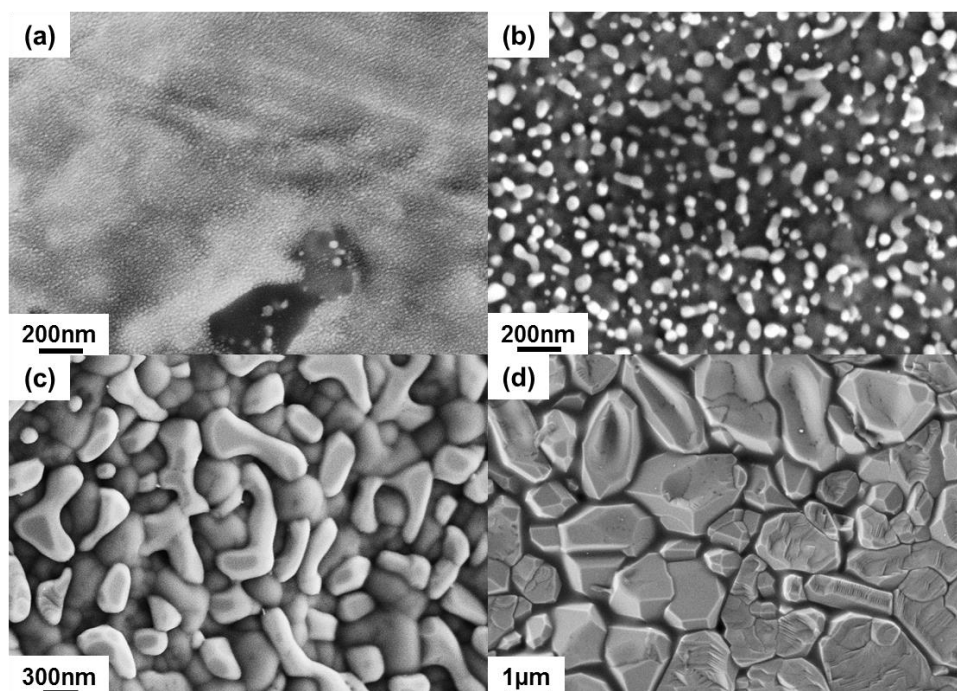


Figure 2.7. SEM plan-view images of oxidized ZrSi_2 at (a) 1000 °C for 5-hours, (b) 1200 °C for 5-hours, (c) 1200 °C for 50-hours and (d) 1400 °C for 5-hours in ambient air.

To understand evolution of oxide layer's surface morphology at high temperatures, XPS analysis was performed. The chemical states of Si, Zr, and O were acquired over a 400 μm diameter circular region on the surface of samples oxidized at each of the temperatures for 5 hours and the results are shown in Figure 2.8. The intensity of Si 2p binding energy peak increases with increasing oxidation temperature - the peak binding energy shifted +1 eV (102.8 eV $\rightarrow$ 103.8 eV) between samples oxidized at 700 °C and those oxidized at higher temperatures (1000 °C and 1200 °C). On the other hand, signal intensity of the Zr 3d_{3/2} and Zr 3d_{5/2} binding energies decreased with increasing oxidation temperature. Here, the peak values shifted - 0.7eV at 1000 °C compared to 700°C (183.6eV $\rightarrow$ 182.9eV). The O1s binding energy associated with the elements showed the same trends with respect to temperature. The intensity of O1s binding energy associated with Zr atom decreased but that of Si atom increased with the binding energy shifts, indicating fundamental differences compositional shifts between 700 °C to 1000 °C/1200 °C exposures. Based on the reported XPS binding energies [43], the binding energy of Si 2p and Zr 3d at 1000 °C and 1200 °C corresponded to SiO_2 and ZrO_2 but those at 700°C did not clearly match with simple oxides. The shifts in x-ray photoelectron peaks are likely associated with a transition in binding states. Such shifts have been reported in a complex mixed oxide (i.e., ZrSiO_4) in comparison to simple oxides (i.e., ZrO_2 and SiO_2) due to different covalency of cations. The Si 2p bonding is more covalent but the Zr 3d is more ionic in ZrSiO_4 [44]. Therefore, it is speculated that at 700 °C a Zr-Si-O phase forms however at 1000 °C and 1200 °C this phase is not stable but rather decomposes to distinct SiO_2 and ZrO_2 simple oxide phases. This is also in good agreement with phase conversion from amorphous ZrSiO_4 film to simple oxides at 900 °C annealing (i.e., $\text{Si-O-Zr} \rightarrow \text{O-Si-O} + \text{O-Zr-O}$) reported in a previous study [45,46]. Interestingly, oxidation product of TiSi_2 at 600 °C in oxygen is glassy Ti-Si-O phase as well [47]. The near-surface chemical composition of oxidized surfaces as determined by the XPS technique is summarized in Table 2.1. The variation of the concentration ratio of Zr to Si indicates that there was not only lateral diffusion of species but also depth-wise diffusion of species. The compositional ratio of Si to Zr was slightly reduced (less Si) at 700 °C but it increased again (more Si) at 1000 °C and gets doubled at 1200 °C compared to the as-received ZrSi_2 . Based

on the published high diffusion rate of Si compared to Zr [48,49], it appears that a part of newly formed Si during oxidation diffused inward in the thin oxide layer so that the Si concentration on the surface is diminished during oxidation at 700 °C. However, a net outward flux of Si atoms at the higher temperatures increases the Si concentration on the outer-most surface.

Table 2.1. XPS near-surface chemical compositional analysis of as-received and ZrSi₂ oxidized at high temperatures.

Atomic %	Si2p	Zr3d	C1s	O1s	Zr:Si
As-polished	32.23	13.59	8.35	45.84	1.0:2.4
700°C for 5hr	21.16	11.40	1.79	65.64	1.0:1.8
1000°C for 5hr	23.38	8.60	3.37	64.65	1.0:2.7
1200°C for 5hr	27.86	6.74	1.69	63.72	1.0:4.1

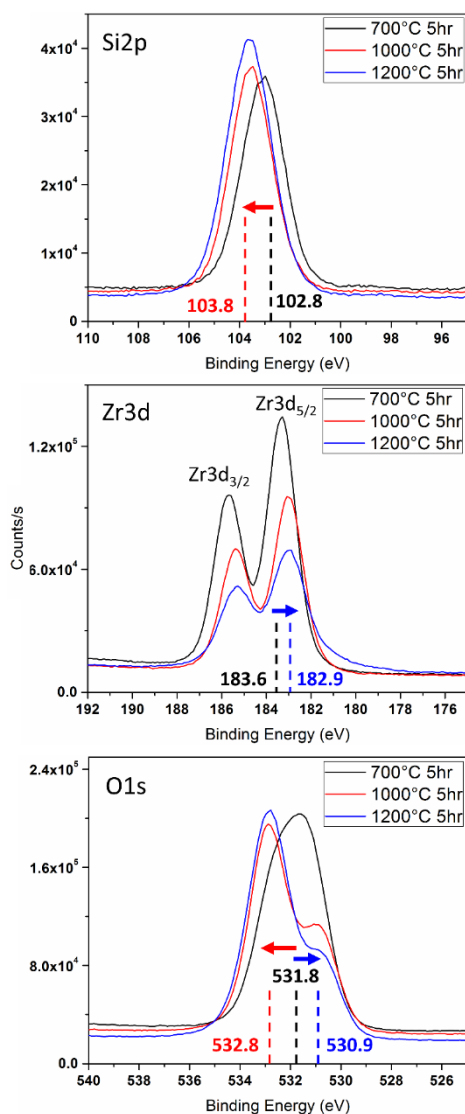


Figure 2.8. XPS spectrum (Si2p, Zr3d, O1s binding energy) of ZrSi₂ oxidized at 700 °C, 1000 °C, and 1200 °C after 5-hour oxidation. Position of the peak maximum (eV) is specified and the arrows indicate the trend in binding energy shift with increasing temperature (from 700 °C to 1000 °C/1200 °C). The red arrows and blue arrows are associated with silicon and zirconium, respectively.

2.1.3. Depth-wise structural evolution of ZrSi₂

In order to correlate the observed surface chemical and morphological evolution with depth-wise species diffusion, cross-sectional analysis using high magnification SEM imaging and STEM imaging was performed (Figure 2.9). A 700 °C, 10-hour oxidation was carried out to get thicker oxide layer and subsequent STEM analysis showed dark wavy structures (Figure 2.9a) in the ~ 630 nm thick oxide layer that formed. EDS line scan analysis showed the structures to be Si-rich oxide phase (Figure 2.9b) and consequently a reduction of Si concentration was identified in the adjacent regions. Based on STEM observations, phase identification by XRD, and the binding energy shift in XPS, the major phases in the oxide layer at 700 °C are likely amorphous and nanocrystalline Zr-Si-O and Si-rich oxide. The cross-sectional images of samples oxidized at 1000 °C and 1200 °C showed complex nano/micron structures. Four types of structures were identified in the 7 µm thick oxide layer formed at 1000 °C: (i) submicron layer with fine structural features, (ii) underlying wavy dark structures, (iii) a thick region consisting of irregular structures, and (iv) unreacted ZrSi₂ region. It is speculated that the wavy structures developed by the inward diffusion of Si in the early stages of oxidation and the non-directional irregular structures were formed by spinodal decomposition in the Zr-Si-O matrix, which will be discussed in detail.

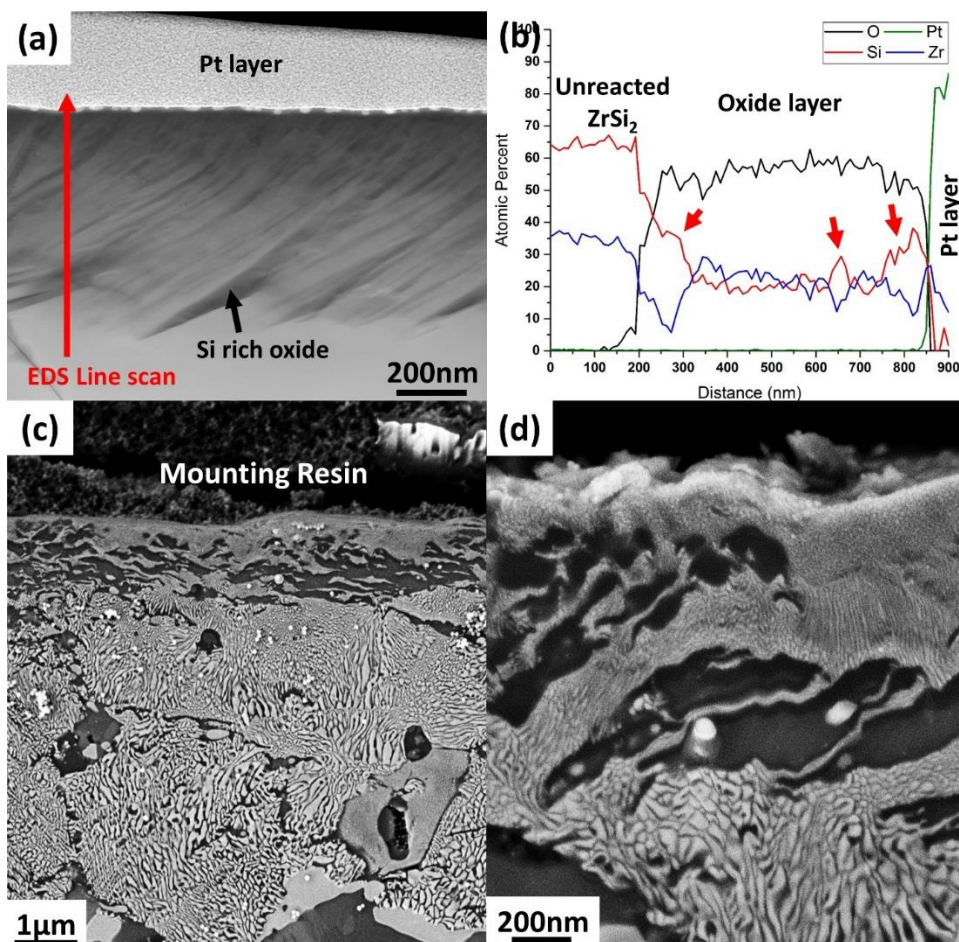


Figure 2.9. (a) HAADF STEM cross sectional image of ZrSi₂ oxidized at 700 °C for 10 hours and (b) corresponding EDS line-scan showing composition fluctuation even in the thin (~630 nm) oxide layer. The red arrows indicate Si-rich oxide. (c) cross sectional SEM image with low voltage (3 kV) of the oxide layer on ZrSi₂ formed at 1000 °C for 5 hours at low magnification and (d) and at high magnification near the top layer.

Similar evolution of oxide structures was observed for samples oxidized at 1200 °C for 5 hours. A large numbers of Si islands indicated by the red arrow in Figure 2.10a were identified at the interface between the oxide layer and unreacted ZrSi_2 . In addition, charging effects were observed in Figure 2.10a, indicating a fully oxidized structure (bright regions) which has dielectric properties. However, some regions appeared not to be oxidized significantly and manifested as dark and grey areas shown in Figure 2.10b. The nanoscale spherical particulates, which was seen on the plan view image, were dispersed only in regions adjacent to air interface (Figure 2.10c). The uniform irregular nanoscale structures were again observed in Figure 2.10d. EDS analysis (Figure 2.11a) showed that the less oxidized regions were composed of Si-rich oxide and unreacted ZrSi_2 . The origin of the Si-rich oxide is the slow reaction kinetics of SiO_2 growth during oxidation of the newly formed Si and some ZrSi_2 was not completely consumed while the oxide layer was developing. The irregular structures seem to consist of ZrO_2 and SiO_2 based on the EDS point scan (point 1 in Figure 2.11b), corresponding to the Si-depleted regions in the EDS mapping. In addition, the existence of Si islands in the interface between the oxide scale and ZrSi_2 suggests that selective oxidation occurs at the high temperatures. Due to relatively large SEM-EDS spot size ($\sim 1 \mu\text{m}$), TEM-EDS analysis was performed to understand mechanism of evolution of this compositionally alternating oxide structure.

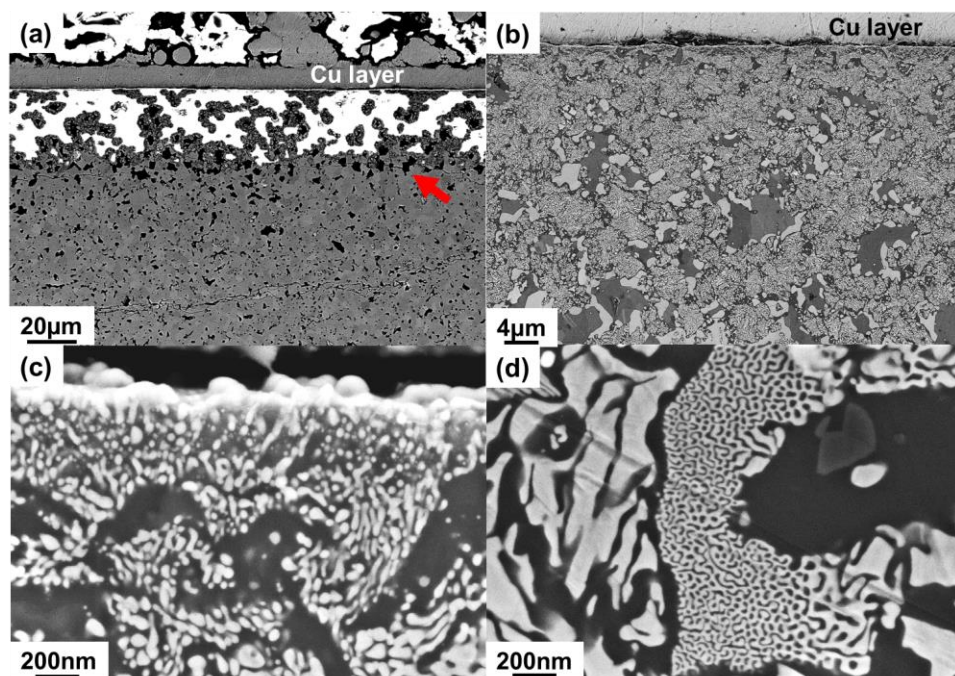


Figure 2.10. SEM images of ZrSi_2 oxidized at 1200 °C for 5 hours, taken at (a) 12kV and (b) 3kV at low magnifications. High magnification 3kV SEM images (c) at interface between air and oxide layer and (d) in the middle of oxide scale showing different shapes of nanoscale structures.

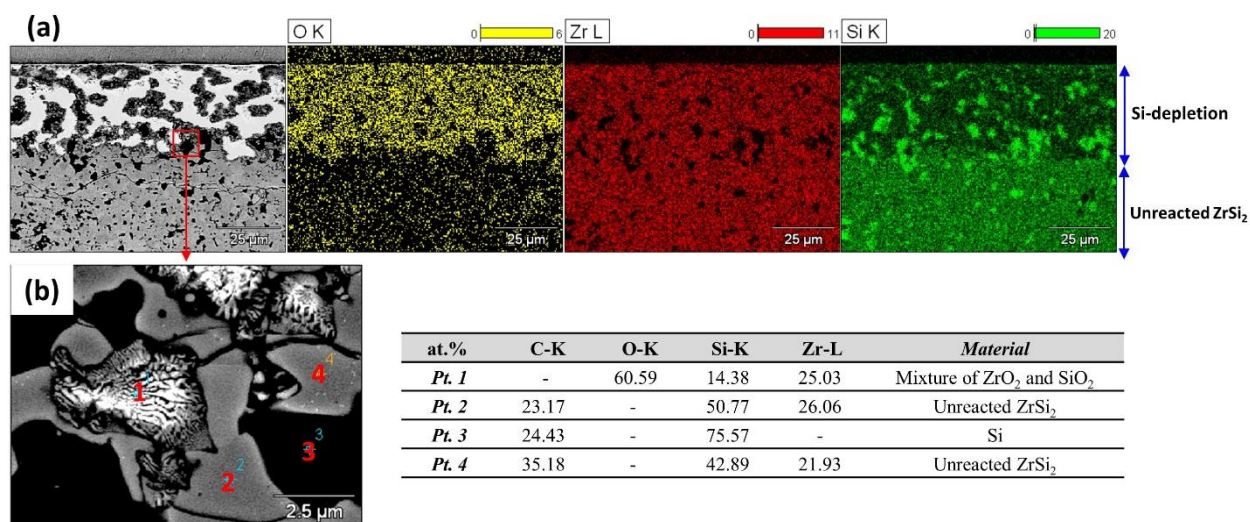


Figure 2.11. EDS spectra mapping (a) of oxidized ZrSi_2 at 1200 °C for 5 hours showing Si depleted region, and point EDS analysis (b) at the interface between oxide layer and unreacted ZrSi_2 . The carbon signal is an artifact from the mounting resin.

The irregular nanoscale structures and spherical phases observed in Figure 2.10c and Figure 2.10d were analyzed using STEM-EDS (Figure 2.12). The high angle annular dark field (HAADF) STEM images of the ZrSi_2 oxidized at 1200 °C for 5 hours revealed nanoscale particulate phases (Figure 2.12a) adjacent to the air interface and the irregular structures (Figure 2.12b) uniformly dispersed in the entire oxide scale. Since brightness in HAADF images is proportional to atomic number of material, it is speculated that the structures were composed of higher atomic number elements compared to the background matrix material. STEM-EDS analysis confirmed the chemical composition of the structures as shown in Figure 2.12c. The spherical particulates and irregular structures were crystalline ZrO_2 in SiO_2 background matrix. The fuzzy ring diffraction pattern (inset, Figure 2.12b) of the background matrix suggests that the SiO_2 phase is amorphous, in agreement with the XRD result where no crystalline SiO_2 peaks were identified.

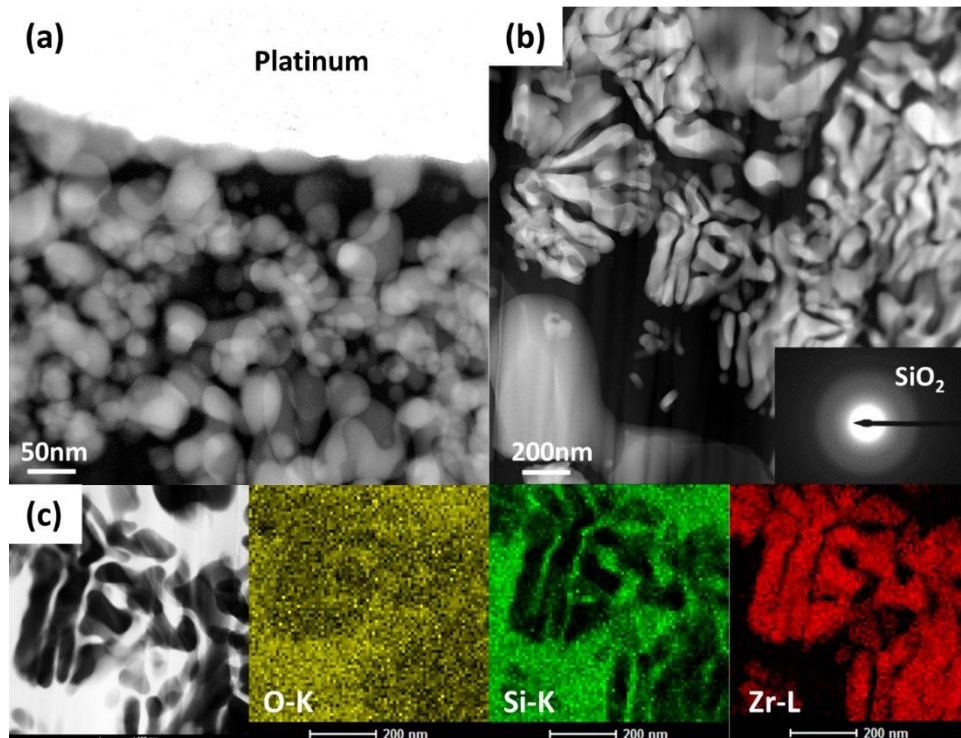


Figure 2.12. HAADF STEM cross sectional images of ZrSi_2 oxidized at 1200 °C for 5 hours. (a) nanoscale spherical phases at the interface with air (i.e., top surface) and (b) irregular structures uniformly dispersed in oxide scale. The inset shows SiO_2 diffraction pattern indicating an amorphous structure. The platinum layer was deposited on the top of the sample during sample preparation by FIB. Higher atomic number material exhibits brighter contrast in these images. (c) Bright field STEM image and STEM-EDS elemental mapping images of the irregular structures. These images clearly indicate the irregular structures consist of ZrO_2 and amorphous SiO_2 .

High magnification SEM image of the near-surface oxidized ZrSi_2 at 1400 °C shown in Fig. 2.13a, indicates distinct layers ZrSiO_4 and SiO_2 . The layers were continuous, suggesting that they are resistant to oxygen diffusion. Underneath the SiO_2 layer, the mixture of zircon, ZrO_2 , and SiO_2 was identified. It is believed that the solid-state reaction to form zircon was not completed. The morphology of the mixture is in good agreement with the literature modeling zircon formation by solid state reaction of tetragonal ZrO_2 and amorphous SiO_2 (Fig. 2.13b) [50].

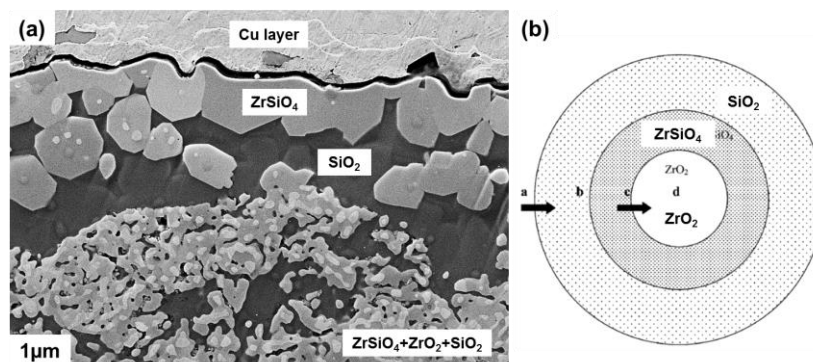


Figure 2.13. (a) SEM cross sectional images of oxidized ZrSi_2 at 1400 °C for 5 hours and (b) schematic diagram of a reaction model for the formation of ZrSiO_4 by a reaction of ZrO_2 and SiO_2 solid phases by Veytizou et al. [50].

2.1.4. Spinodal Decomposition of ZrSi₂ at 1000 °C and 1200 °C

As mentioned earlier, a plausible explanation to the formation of an alternating nano-layered structure of ZrO₂ and SiO₂ is phase separation of Zr-Si-O phase by spinodal decomposition, a diffusion driven process that occurs in unstable undercooled or supersaturated phases, resulting in homogenous two-phase fine scale mixture. Lucovsky et al. first reported that annealing of ~400 nm amorphous ZrSiO₄ thin film at 900 °C for 60 seconds led to chemical phase separation consisting of crystalline ZrO₂ and amorphous SiO₂ based on infrared absorption spectroscopy [45,46]. A thermodynamic driving force exists if the solid mixture is within unstable spinodal boundary. Kim et al. estimated the excess Gibbs free energy of mixing in supercooled liquid of ZrO₂ and SiO₂ using a subregular model utilizing the invariant points in pseudo-binary ZrO₂-SiO₂ phase diagram [51]. In addition, Stemmer et al. predicted extension of the liquid miscibility gap and spinodals to lower temperature using commercially available thermodynamic software and published oxide data [52]. Based on their estimations, the composition of spinodal boundary between 1000 °C and 1200 °C in ZrO₂ and SiO₂ mixture is in the range of 0.4~0.9 SiO₂ mole fraction and its corresponding decomposed equilibrium phases are ZrO₂ rich phase (0.2~0.4 SiO₂ mole fraction) and SiO₂ rich phase (0.9~0.98 SiO₂ mole fraction). Therefore, it is suggested that there is a thermodynamic driving force that induces spinodal decomposition in ZrSi₂ oxidation at high temperatures.

At 1000 °C, the spinodal structures near the top surface were finer than those at the center of the oxide layer, which may be attributed to ZrO₂/SiO₂ composition effect on Gibbs free energy of mixing. The minimum wavelength of phase modulation decreases with increasing negative values of second derivative of Gibbs free energy of mixing [53]. The absolute value of the negative free energy is maximized at 73% mole fraction of SiO₂ at 1000 °C calculated by the subregular model proposed by Stemmer et al., which is consistent with Si concentration of the 1000 °C surface, resulting in formation of the finer spinodal structures.

Additionally, nucleation of the ZrO₂ particulates at 1200 °C on the top surface would also be explained by the extension of the liquid miscibility gap. Due to the highest concentration of SiO₂ on the top surface by outward Si diffusion in oxide layer at 1200 °C, the composition may not be within the spinodal boundary but within miscibility gap. Therefore, nucleation and growth of ZrO₂ in SiO₂ matrix will likely lower its free energy *in lieu* of spinodal decomposition.

2.1.5. Kinetic Suppression of Crystalline ZrSiO₄ Formation

It is worth noting that crystalline ZrSiO₄ was not identified in the ZrSi₂ oxidation at 1000 °C for 10 hours and 1200 °C for 5 hours even though its formation is preferred as indicated in binary ZrO₂-SiO₂ phase diagram at either temperature with any composition. However, the phase identification of ZrSiO₄ at longer oxidation (1200 °C for 50 hours) and higher temperature oxidation (1400 °C for 5 hours) of ZrSi₂ agree with published results that ZrSiO₄ formation from a reaction of ZrO₂ and SiO₂ requires at least 1300°C annealing temperature [50,54–56]. Formation of crystalline ZrSiO₄ is a solid state reaction – it is hypothesized that Si⁴⁺ cations from amorphous SiO₂ diffuse through the highly refractory ZrSiO₄ layer and reacts with t-ZrO₂ in order to produce new phase and there are no mobile liquid or gas species [50]. Therefore, the growth rate of crystalline ZrSiO₄ is kinetically limited although it is thermodynamically favored.

2.1.6. Summary of ZrSi₂ Oxidation

Based on the analysis in this study, a physical model for microstructural evolution during the isothermal oxidation at each test temperature has been developed and is schematically shown in Figure 2.14 to understand microstructural evolution in the oxide layer. At 700 °C, a thin oxide layer consisting of Zr-Si-O phase matrix with Si-rich oxide wavy structures forms. Additionally, small amount of Si and ZrO₂ was identified in XRD analysis. The role of the newly formed Si by the selective oxidation in ZrSi₂ is important. The Si diffuses around the oxide layer and leads to the formation of Si-rich spherical phases on the surface

and its inward diffusion induced reduction of Si concentration in the top surface while promoting the formation of Si-rich wavy oxide. Although the composition of the oxide is within the estimated spinodal boundary, mobility of species at this temperature is not enough to show distinct phase separation.

At 1000 °C, in the initial stages of oxidation, the Si diffused inward first when it reacted with oxygen in the thin oxide layer and agglomerated resulting in wavy Si rich oxide structures. The wavy structures seen in 700 °C oxidation tests were likely precursors of those observed at 1000 °C. While oxidation continues, outward diffusion of the newly formed Si dominates as confirmed by the increment of Si concentration at the surface. In the oxide/ZrSi₂ interface, the amorphous Zr-Si-O mixture decomposed quickly so that the isotropic irregular structures consisting of ZrO₂ and SiO₂ were generated. At the same time, the Si produced Si-rich oxide islands near the spinodal structures.

At 1200 °C, the oxidation behavior was similar to that at 1000 °C except for the nucleation of the nanoscale ZrO₂ particulates near the air interface. Due to remarkable outward diffusion of Si ions, the Zr-Si-O mixture was metastable and reduced its free energy by ZrO₂ nucleation. During short time oxidation, an intermediate unstable Zr-Si-O mixture exists which undergoes phase separation to ZrO₂ and SiO₂.

At 1400 °C, crystalline ZrSiO₄ phase develops through solid-state reactions between ZrO₂ phases and SiO₂ phases, resulting in the formation of continuous ZrSiO₄ layer on the top of the oxide scale. Surplus SiO₂ phases in the reaction for ZrSiO₄ remain as a thin layer underneath the ZrSiO₄ layer. Due to the excellent oxidation resistance of the two layers, oxidation process becomes so slow that thickness of the whole oxide scale is thinner than that formed at 1200 °C. The solid-state reaction continues in the middle of the oxide layer so that a mixture of ZrO₂, SiO₂, and ZrSiO₄ phases and islands of SiO₂ coexist.

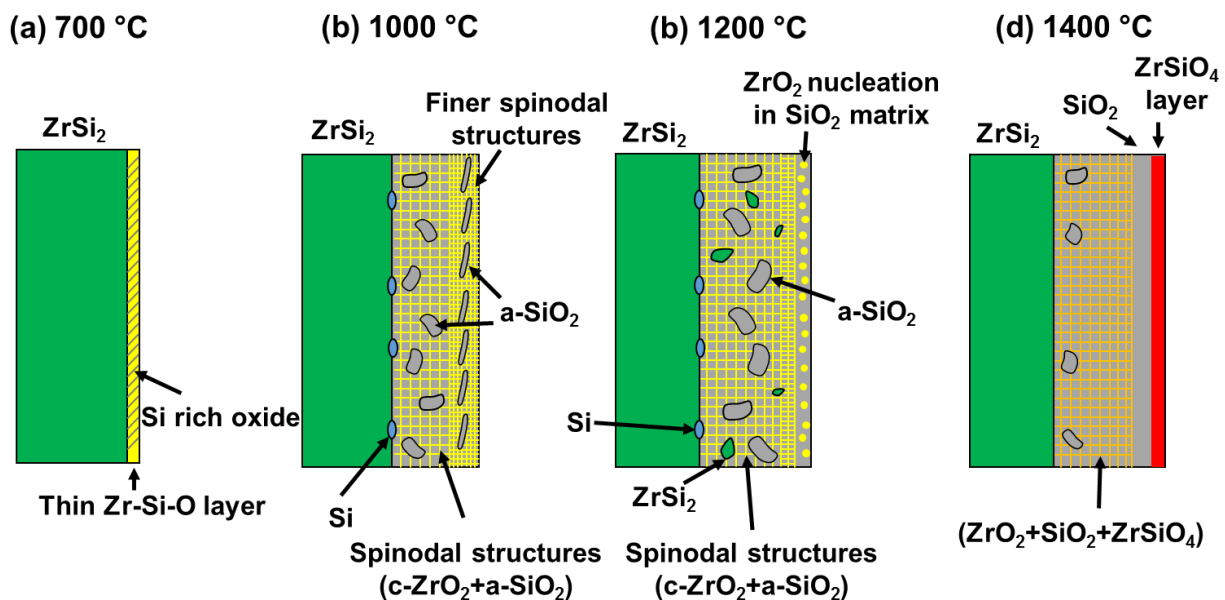


Figure 2.14. Schematic illustration of the microstructural evolution during isothermal oxidation of ZrSi₂ oxidation at (a) 700 °C, (b) 1000 °C, (c) 1200 °C, (d) 1400 °C. c=crystalline and a=amorphous. The features in the figures are disproportionately scaled for clarity.

2.1.7. Oxidation of Zr₂Si at 1200 °C

Oxidation behavior of one of Zr-rich silicides, Zr₂Si, was investigated by characterization after oxidation at 1200 °C for 1 hour. The behavior may be different from Si-rich silicide (ZrSi₂). As shown in the photograph in Figure 2.15, the Zr₂Si samples got completely crumpled during the oxidation while the

ZrSi₂ samples maintained their rectangular shape. This confirms in a very practical sense, the expected result that ZrSi₂ is superior to Zr₂Si in terms of oxidation resistance and mechanical integrity in high temperatures.

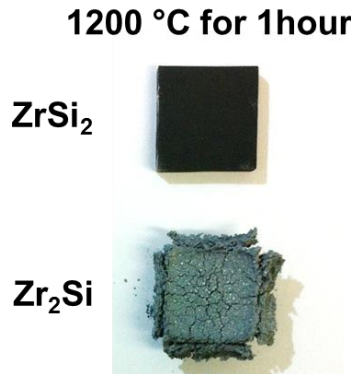


Figure 2.15. Photograph showing the oxidized ZrSi₂ and Zr₂Si after oxidation at 1200 °C for 1 hour in air.

The cross-sectional SEM images of a small particle of the oxidized Zr₂Si are shown in Figure 2.16. Most regions of the Zr₂Si particle were oxidized heavily and a large amount of ZrO₂ had formed as manifested in the charged area of the image (bright area) in Figure 2.16a. The less oxidized regions at the center were identified as newly formed ZrSi₂ by the compositional analysis. Moreover, only monoclinic-ZrO₂ and ZrSi₂ phases were identified in XRD analysis as shown in Figure 2.16d. The origin of material disintegration appeared to be crack propagation in ZrO₂ regions (see Figure 2.16b). The tetragonal-ZrO₂ formed during Zr₂Si oxidation at 1200 °C underwent phase transformation to monoclinic-ZrO₂ upon cooling, resulting in significant compressive stresses due to volume increase. A similar failure morphology was also observed in Zirc-4 oxidized at 1200 °C. In addition, the spinodal structures were also confirmed as shown in Figure 2.16c but only limited area near ZrSi₂ regions, differing from the ZrSi₂ oxidation. Based on the experimental data, the postulated oxidation reaction of Zr₂Si at 1200 °C is as follows:



Subsequently, the newly formed ZrSi₂ decomposed into crystalline ZrO₂ and amorphous SiO₂ so that the spinodal structures were only observed near ZrSi₂ regions as discussed in detail in the previous section.

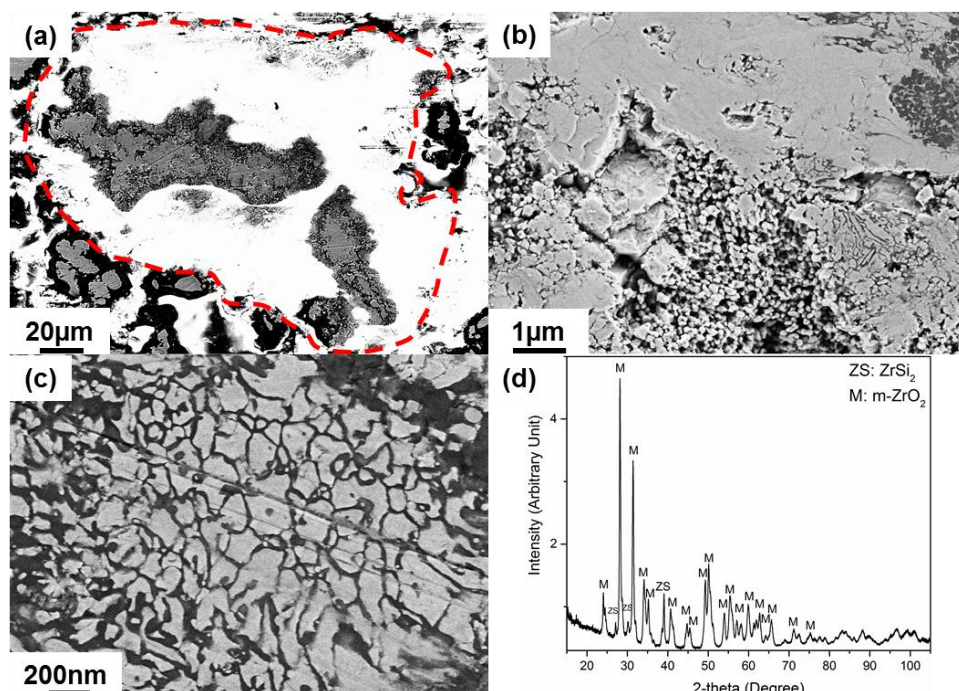


Figure 2.16. Cross-sectional SEM images of a ZrSi_2 samples oxidized at 1200 °C for 1 hour. (a) Red dots in the high voltage (12kV) SEM image indicate the particle boundary, (b) cracks leading to structural disintegration were identified in ZrO_2 region, and (c) spinodal structures are seen locally near ZrSi_2 phase. (d) Full-theta X-ray diffraction (XRD) peaks of the ZrSi_2 oxidized at 1200 °C for 1 hour in air.

2.2. Pressurized Steam Corrosion Test

Oxidation of bulk ZrSi_2 at high temperatures was investigated as reported in the last section, but potential materials for protective coating on Zr-alloy cladding should maintain or improve corrosion resistance under normal reactor operation conditions as well. The improved corrosion resistance by protective surface coatings at normal operating temperatures such as 300 to 320 °C for PWRs and 250 to 300 °C for BWRs would reduce overall oxidation and hydriding of the Zr-alloy cladding, resulting in extension of allowable fuel burn-up and improved economics [57]. Therefore, material behavior of bulk ZrSi_2 in high pressure water/steam conditions prototypic of corrosion in normal LWR operating conditions were characterized by SEM-EDS and is discussed in this section.

2.2.1. Water Autoclave Test at Westinghouse Electric Company

Polished bulk ZrSi_2 samples were shipped to Westinghouse Electric Company (WEC, Pittsburgh PA) for water autoclave corrosion tests. For these tests, the samples were exposed in pure water at 330 °C in 18.6 MPa for 72 hours. The metallic surfaces of the samples before the corrosion (Figure 2.17a) changed to white color (Figure 2.17b) and degraded during the test.

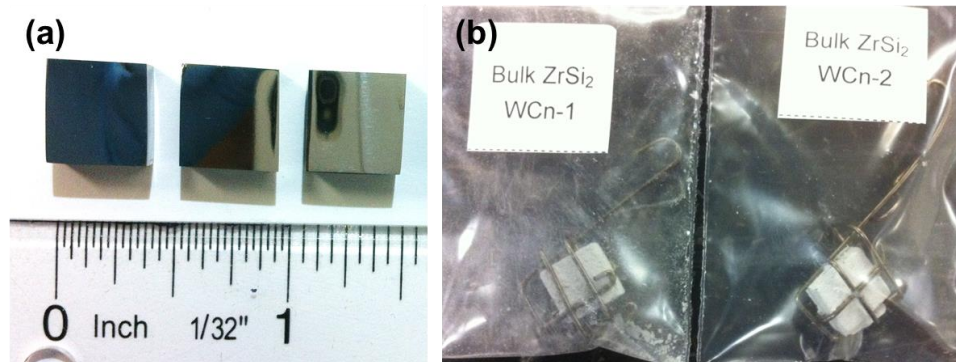


Figure 2.17. Photographs of (a) as-polished bulk ZrSi₂ before corrosion test at 330 °C and 18.6 MPa in pure water for 72 hours and (b) the samples after the autoclave test.

Plan-view SEM images of the bulk ZrSi₂ samples before and after the autoclave test are shown in Figure 2.18. After the test, surface morphology became rough and cracked. The near-surface region of the material was disintegrated and pores and debris were observed on the surface. It is speculated that formation of the pores is related to the preexisting free silicon impurities in the ZrSi₂ matrix which subsequently got leached out during the corrosion tests.

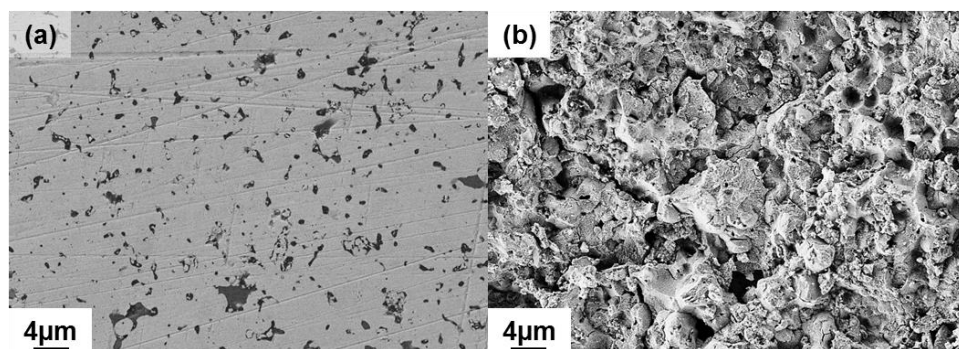


Figure 2.18. SEM plan-view images of (a) as-polished ZrSi₂ and (b) ZrSi₂ after 330 °C, 18.6 MPa water corrosion test.

SEM cross-sectional images of the corroded ZrSi₂ samples is shown in Figure 2.19. Thickness of the oxide layer formed during the corrosion test was approximately 40 μm and displayed as very bright region as shown in Figure 2.19a due to dielectric properties of ZrO₂. In the local cross-sectional area underneath the oxide layer, micron-size pores in the ZrSi₂ matrix were identified (Figure 2.19b), which is consistent with the pores observed in the plan-view images. Again, it appears that the pores were originally free silicon grains present as impurities. In addition, thin darker boundaries were observed at the interfaces between the corroded regions and the unreacted regions, and the corroded area revealed nano-scaled porous structures. The darker boundaries may be a silicon-rich layer, related to corrosion process of ZrSi₂ in high temperature, pressurized water. Thin silicon-dioxide layer has been reported in high temperature corrosion of CVD-SiC in moisture containing air at 1200 °C and 1 MPa after testing for 500 hours [58]. The layer was identified between porous silica scale and unreacted SiC matrix. It is believed that the porous structure forms due to loss of silicon in the ZrSi₂ matrix because the EDS elemental mapping for cross-section of the sample shows a small concentration of silicon (Figure 2.20a). Only 7 to 8 at. % of silicon was detected in the corroded region (point 1, 2, and 3 in Figure 2.20b) and the major phase present in the corroded region is ZrO₂.

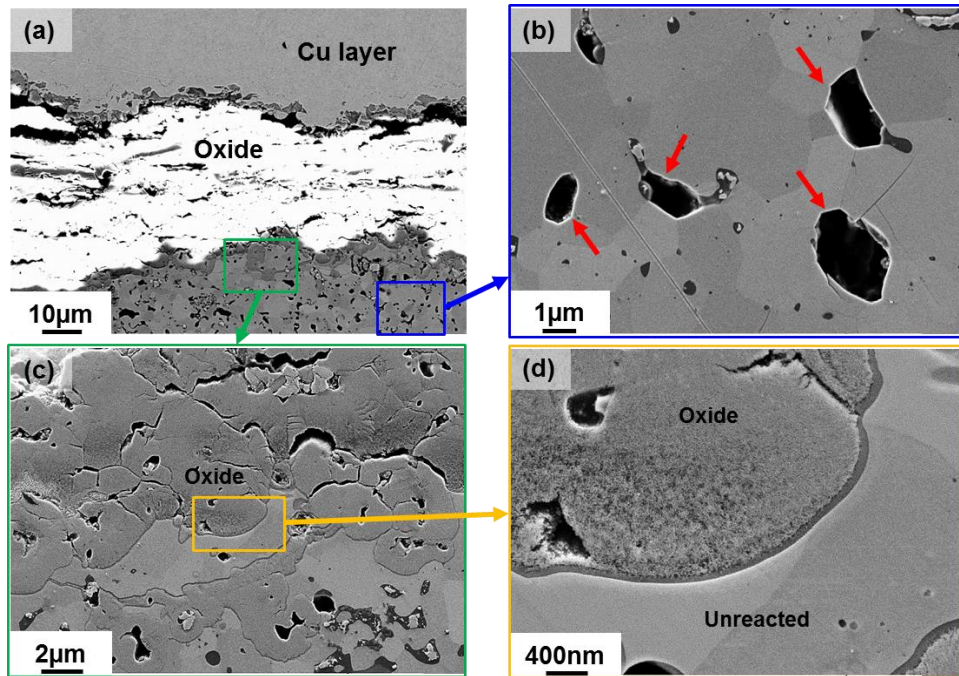


Figure 2.19. Cross-sectional SEM images of bulk ZrSi_2 after the water corrosion tests at 330 °C and 18.6 MPa for 72 hours: (a) low magnification, and (b-d) local areas with high magnifications. The red arrows indicate pores in ZrSi_2 matrix.

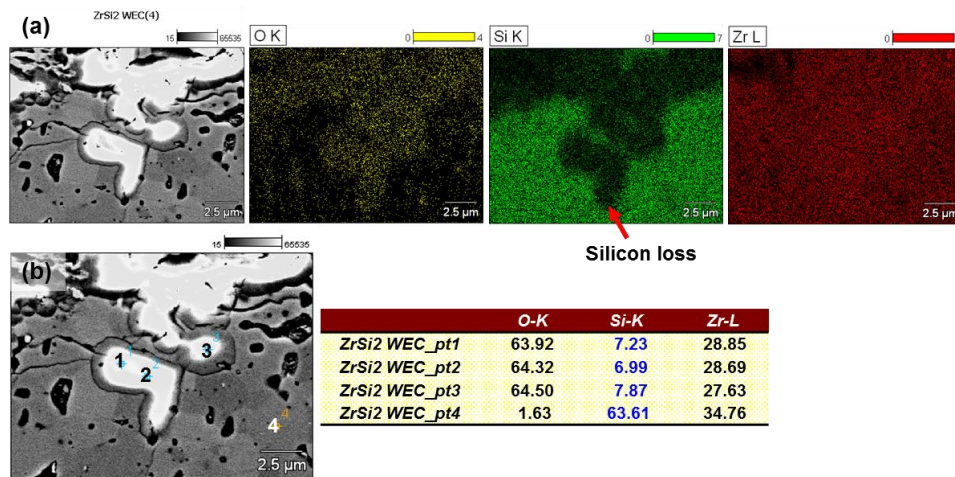


Figure 2.20. EDS analysis of cross-section of bulk ZrSi_2 after the water corrosion test at 330 C and 18.6 MPa for 72 hours: (a) elemental mapping and (b) elemental point scan.

2.2.1. Steam Autoclave Test at UW-Madison

Steam corrosion tests for bulk ZrSi_2 were conducted at UW-Madison to investigate how this environment compares with the water corrosion test performed at WEC. Single crystal silicon flats and Zirc-4 flats were polished using 320, 400, and 600 SiC abrasive papers and introduced in the autoclave as reference samples. Bulk ZrSi_2 and bulk Si samples were pre-oxidized in ambient air at high temperatures to demonstrate effect of surface oxidation on silicon loss. The oxidation conditions were 700 °C for 100 hours and 1400 °C for 5 hours for both sample materials. The oxidation processes resulted in thin oxide layers on the silicon samples as shown in Figure 2.21. Based on XRD patterns, phase of the oxide scale

produced at 700 °C and 1400 °C air was quartz SiO_2 and cristobalite SiO_2 , respectively. As presented in the last section, bulk ZrSi_2 formed a thin oxide layer consisting of Zr-Si-O and SiO_2 at 700 °C and thin oxide layer containing ZrSiO_4 and 1400 °C in ambient air.

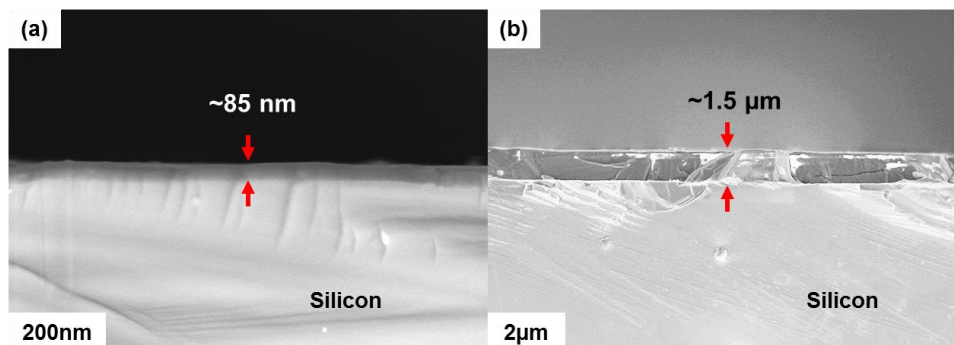


Figure 2.21. Formation of thin oxide layers on bare silicon surface after high temperature oxidation at (a) 700 °C for 100 hours and (b) 1400 °C for 5 hours. The images are SEM cross-sectional fracture surface images.

All samples were exposed in high temperature steam (400 °C) at 10.3 MPa for 72 hours, and deionized pure water (18 MΩ) was flowed into the test chamber with a slow flow rate (~ 5 ml/min). The weight changes for the samples after the steam test are summarized in Figure 2.22. All samples showed weight loss after corrosion test except for bare Zirc-4. The weight of the bare and oxidized silicon samples decreased significantly after the test indicating that silicon loss in ZrSi_2 matrix is a primary factor for the weight reduction. While the corrosion of silicon species in ZrSi_2 occurs by removal of silicon atoms on the surface under pressurized steam, zirconium species in ZrSi_2 would be oxidized and remains as ZrO_2 . Spallation of thin oxide layer was identified on the oxidized samples at 1400 °C for 5 hours by visual inspection, resulting in the largest weight reduction in Figure 2.22. It appears that the weight loss decreased after pre-oxidation at 700 °C in ZrSi_2 (58%) and Si (20%) samples compared to the as-polished samples but an explanation to this observation is not clear.

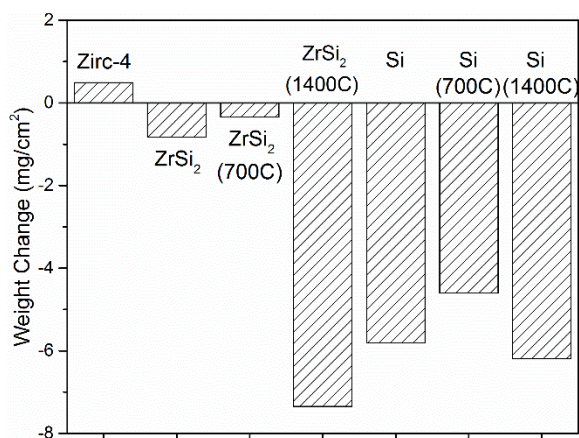


Figure 2.22. Weight change for bare Zirc-4, ZrSi_2 , Si, and pre-oxidized samples (700 °C for 100 hours and 1400 C for 5 hours) after the steam test at 400 °C and 10.3 MPa for 72 hours.

The plan-view SEM images for the bare ZrSi_2 and the pre-oxidized ZrSi_2 at 700 °C after the steam autoclave test are shown in Figure 2.23. As presented in the water corrosion test in Westinghouse Electric Company, the bare ZrSi_2 surface after the steam test revealed surface cracks and pores. Again, the silicon

impurities in the ZrSi_2 matrix may be leached out during the steam corrosion and leave pores on the surface. Mechanical integration of the top surface was so weak that a significant number of debris particulates were detected on the surface. On the other hand, the pre-oxidized surface was smoother and cleaner than the bare ZrSi_2 surface. Surface pores were observed in the images but severe cracks and local spallation of oxide layer were not observed. The observation is consistent with results of the weight gain plot that the pre-oxidation mitigated the weight loss. Therefore, the pre-oxidized surface was relatively stable under the high temperature steam environment compared to the bare ZrSi_2 . Nevertheless, the top surface of the pre-oxidized ZrSi_2 after the steam test showed the nano-scaled pores as shown in Figure 2.24a. Significant reduction of silicon concentration on the surface in the EDS result (Figure 2.24b) supports a hypothesis that material degradation of ZrSi_2 (cracks and porous structures) is caused by a loss of silicon species by an interaction of ZrSi_2 and water.

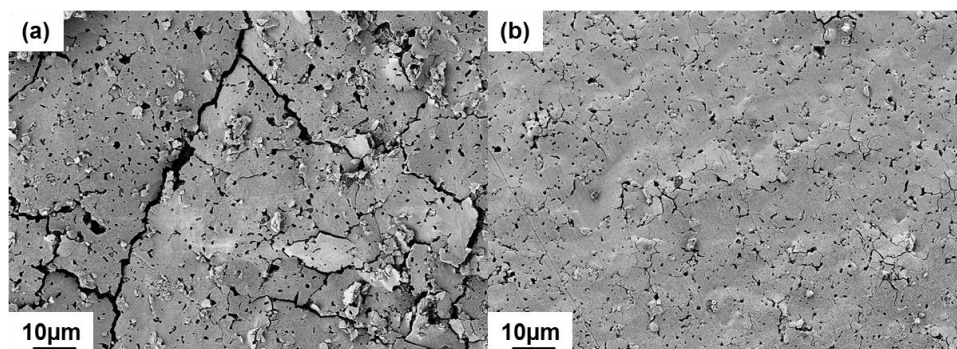


Figure 2.23. SEM plan view images for (a) bare ZrSi_2 and (b) pre-oxidized ZrSi_2 (700 °C for 100 hours in ambient air) after steam corrosion test at 400 C and 10.3 MPa for 72 hours.

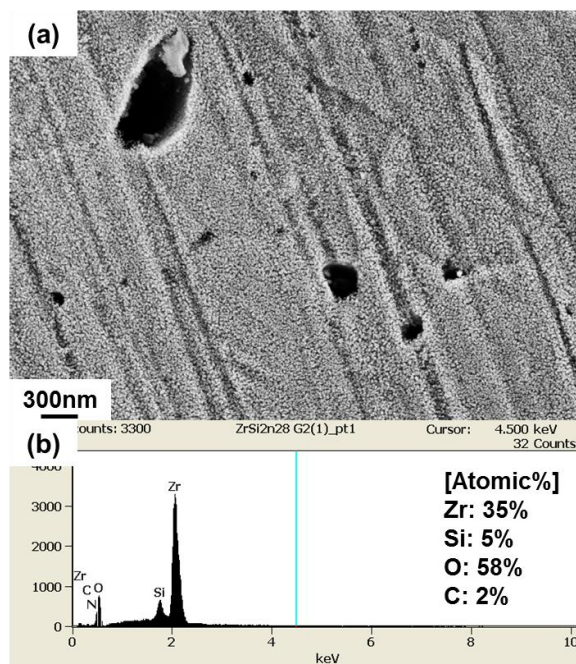


Figure 2.24. (a) High magnification SEM plan-view image of pre-oxidized ZrSi_2 (700 °C for 100hrs) after the steam autoclave tests (400 °C, 10.3 MPa for 72 hrs) and (b) results of corresponding EDS average scan.

The weight loss for the silicon samples is confirmed by SEM imaging of the samples after the steam corrosion test as shown in Figure 2.25. The high temperature steam reacted with the samples so that distinct surface morphologies were displayed. Before the steam corrosion test, all the silicon samples were smooth and the only surface features were identified were polishing marks. The oxygen concentration increased with increasing temperature of the pre-oxidation in ambient air. On the contrary, the surfaces become rough and noticeable surface features were identified after the corrosion test. For example, the high temperature steam attacked preferential area on the pre-oxidized surface (700 °C for 100 hours in air), resulting in the micron-scaled triangular surface features (Figure 2.25d). In addition, the network of micron cracks on local area of pre-oxidized silicon (1400 °C for 5 hours in air) was identified as shown in Figure 2.25f. The oxide scale was not fully consumed, but rather grain boundaries of cristobalite SiO_2 scale would be attacked under the steam environment. It appears that the grain boundary attack weakened mechanical integrity of the oxide layer, resulting in local spallation of the top layer associated with the large weight loss. Moreover, oxygen concentration on the bare Si surface and the oxidized Si surface at 700 °C decreased after the corrosion. This indicates that surface recession on the Si samples with removal of the thin oxide layer occurred under the high temperature steam environment.

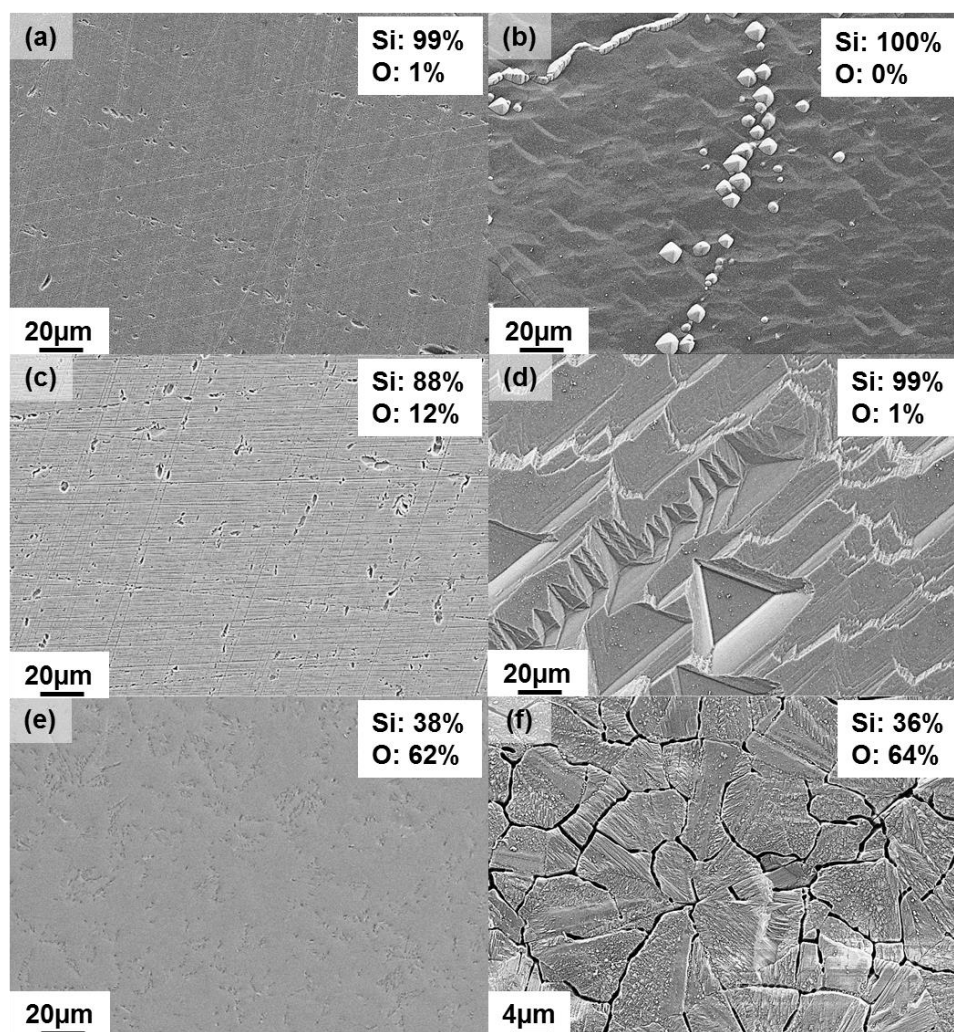
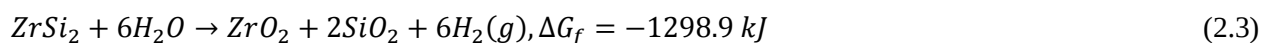


Figure 2.25. SEM plan-view images of (a) bare Si, (b) bare Si after steam test, (c) pre-oxidized Si at 700 °C for 100 hours, (d) pre-oxidized Si (700 °C) after the steam test, (e) pre-oxidized Si at 1400 °C for 5 hours, and (f) pre-oxidized

Si (1400 °C) after the steam test. The steam test was performed at 400 °C and 10.3 MPa for 72 hours in pure water. The silicon and oxygen atomic percent on each surface are specified.

The loss Si from bulk ZrSi₂ and Si samples in the water/steam environment was not observed in high temperature air. Another example for water vapor effects on oxidation of transition metal silicides is presented by Wood et al. [59] The authors reported that MoSi₂ displayed different oxidation behavior in water vapor environment than in dry air. The tests were performed under atmospheric pressure. Mass gain of MoSi₂ in 75% water vapor at 600 °C was approximately 100 times higher than that in dry air condition. Moreover, the oxidized samples in water vapor displayed swelling and warping. It was believed that the water vapor inhibited formation of a uniform SiO₂ layer for passivation. It is speculated that increased solubility of SiO₂ in water, formation of gaseous silicon hydroxide and gaseous SiO phase at elevated pressures and temperatures in water environment are responsible for the weight loss and the surface recession of the ZrSi₂ and Si materials. First, the postulated reaction between ZrSi₂ and H₂O at 400 °C is as follows:



The reaction products (zirconia and silica) should have a dense microstructure and good adhesion to base material to act as a passive layer. However, SiO₂ is dissolved by water to some extent. Fournier and Rowe measured concentration of dissolved SiO₂ species in water during high pressure autoclave test using a colorimetric method and reported that solubility of amorphous SiO₂ in pure water increased exponentially with increasing water temperature at the vapor pressure of the solution [60]. A linear relationship between the solubility and system pressure at constant temperature (i.e., 200 °C) was observed. In addition, volatility of SiO₂ would contribute to degradation of surface oxide layer in ZrSi₂ in water environments. Opilia et al. concluded that volatilization of SiO₂ below 1300 °C was dominated by equation 2.4 with linear kinetics [61].



Silica-forming structural materials like SiC show the weight loss material recession as well. As presented by Terrani et al., [60] SiO₂ layer formed on CVD SiC surfaces contained significant porosity under high pressure and high temperature steam environment (1200 °C and 0.34 to 2.07 MPa) so that material recession rate was an order of magnitude higher than atmospheric pressure conditions. Finally, non-protective SiO is formed if the oxygen partial pressure is very low even in the presence of water, leading to rapid material recession.

2.2.2. Immobilization of Silicon in Water Corrosion

The zircon (ZrSiO₄) formed ZrSi₂ surface was the only condition in which the silicon concentration remained constant after steam corrosion test. As shown in Figure 2.26a, the surface maintained the original surface morphology of dense and micron sized ZrSiO₄ grains except for many etch pits around the grain boundaries. Moreover, spallation of the zircon layer on the local surface was revealed, being related to the weight loss. Even though zircon is one of the most corrosion resistant materials under water conditions [62], it seems that corrosion started at grain boundaries with elimination of silicon species and weakened mechanical integrity of the zircon layer. Ueno et al. also reported the same phenomenon during static water corrosion test (1300 °C for 100 hours) for bulk zircon samples [63]. The authors observed that amorphous SiO₂ rich phases present in the grain boundaries from silicate compounds, and the grain boundaries were easily corroded by water vapor. EDS results (Figure 2.26b) showed that silicon loss on the oxidized surface was prevented. Thus, our studies demonstrate that forming a zircon layer is highly effective in immobilizing Si in normal LWR water environments, however for this to be a practical solution the compactness of the zircon grains must be improved (minimizing surface area of grain boundaries).

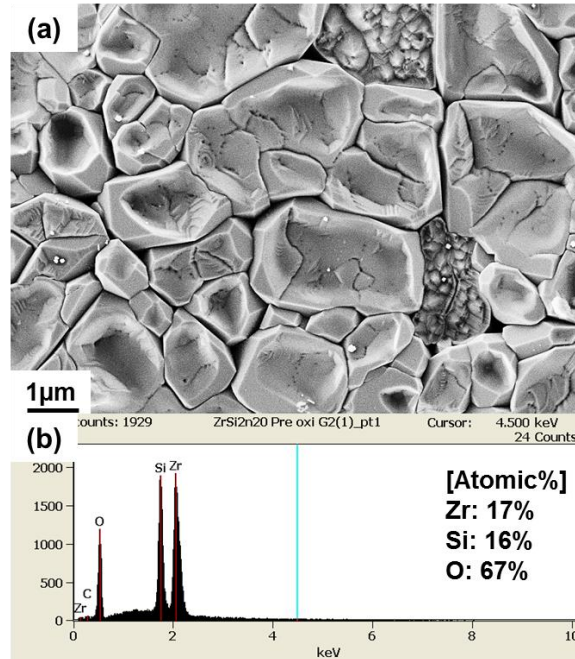


Figure 2.26. (a) SEM plan-view image of pre-oxidized ZrSi_2 (1400 °C for 5 hours in air) after the steam corrosion test at 400 °C at 400 °C and 10.3 MPa for 72 hours in pure water, and (b) results of EDS chemical analysis for the corresponding area.

Chapter 3: Development of Magnetron Sputter Zr-Si Coatings

3.1. Parametric Investigation of Coating Quality

Investigation of magnetron sputter deposition process to fabricate zirconium-silicide coating as a protective barrier under extreme conditions was performed. Process parameters such as deposition power, sputtering gas pressure, and samples surface preparation determine coating quality and efficiency of deposition process. To the best of author's knowledge, experimental data for magnetron sputter process for zirconium-silicide coatings has not been reported so optimization of deposition parameters was conducted, and the results are presented and discussed in this section.

3.1.1. Deposition Parameters

The dc sputter power was determined to be linearly proportional to a sputter yield rate (the number of ejected atoms per incident ion), as shown in Table 3.1, indicating that higher sputter power is beneficial to deposit desired thickness more rapidly. However, sputter targets experience significant thermal stress as increasing sputter power can cause target failure, particularly for ceramic targets. For example, a ZrSi_2 sputter target was damaged at 160 W. To eliminate this problem, sputter power was lowered to 135W and a copper plate was bonded on the backside of the target to accommodate the thermal shock.

In addition, it was found that the deposition rate for ZrSi_2 sputter coating at a constant sputter power was inversely proportional to pressure of sputtering gas (i.e., argon gas) as shown in Table 3.2. The deposition rate was measured by a crystal monitor in the vacuum chamber and is a relative value.

Table 3.1. Deposition rate of ZrSi_2 coating at 10 mtorr Ar pressure as a function of sputter power.

Sputter power (W)	Deposition rate ($\text{\AA}/\text{s}$)
90	0.63
135	0.89
160	1.1

Table 3.2. Deposition rate of ZrSi_2 coating at 135 W sputter power as a function of Ar pressure.

Argon pressure (mtorr)	Deposition rate ($\text{\AA}/\text{s}$)
4	1.07
6	1.02
8	0.97
10	0.89
12	0.83

As shown in Figure 3.1a, local areas of the as-deposited sputter coating of ZrSi_2 displayed coating delamination. This may be attributed to residual compressive stress and a weak adhesion to the Zirc-4 substrate due to native oxide layer on the surface and surface contamination. To enhance coating adhesion to the substrate, the bare Zirc-4 flats were subjected to in-situ plasma cleaning (dc 500W for 5 minutes under 1.6 Pa argon pressure) prior to initiating the coating deposition process in the sputter chamber. Figure 3.1b shows that yellowish surface color of the bare Zirc-4 flat changed to the metallic surface color after the plasma cleaning. After the effective removal of surface contamination, defects on surface of coatings were not identified. This cleaning process was performed for all Zirc-4 substrates before deposition of zirconium-silicide coatings.

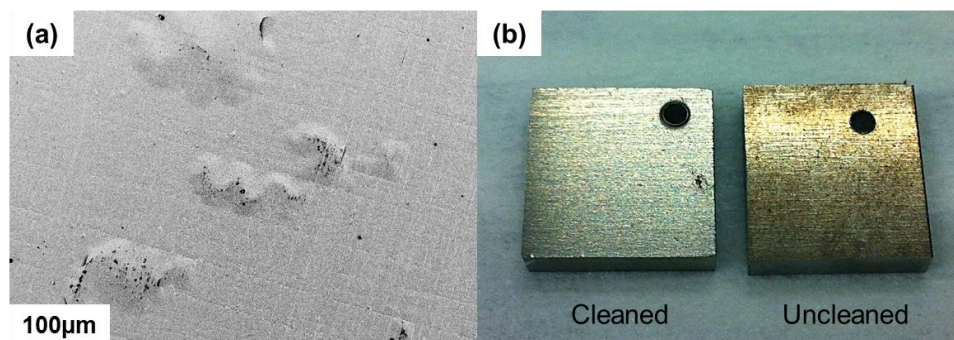


Figure 3.1. (a) SEM image of ZrSi_2 coating without the plasma surface cleaning of Zirc-4 substrate and (b) photograph of Zirc-4 flats after plasma surface cleaning.

Surface morphology and cross-sectional microstructure of the coatings were examined and investigated using SEM. The coatings showed uniform and smooth surface with no indication of spallation. Argon gas pressure influenced microstructure significantly as shown for example for ZrSi_2 in Figure 3.2. The ZrSi_2 coating deposited at higher argon pressure (i.e., 1.33 Pa) exhibited relatively rougher surface and showed nanometer scale gaps in the microstructure (Figure 3.2a). Cross-sectional fracture surfaces of these coatings deposited on Si substrate showed tapered columnar microstructures which are revealed more clearly in Figure 3.2c. In contrast, at the lower argon pressure (i.e., 0.53 Pa) the ZrSi_2 coating exhibited short and dense columnar structures with smoother surface, which are shown in Figure 3.2b and Figure 3.2d. The observation is in good agreement with Thornton's model suggesting that the columnar tapered morphology of the films is a result of atomic shadowing and a low mobility of sputtered atoms on the growing surface at low temperatures [31]. In addition, this morphology would be promoted by increased scattering between argon atoms and target atoms at higher argon pressures. It is expected that the nanoscale gaps between the long columnar structures at the higher argon pressure may act as paths for the transport of oxygen to the underlying Zirc-4 substrate during the oxidation tests. Therefore, all coatings for oxidation tests were prepared at the low argon pressure (0.53 Pa).

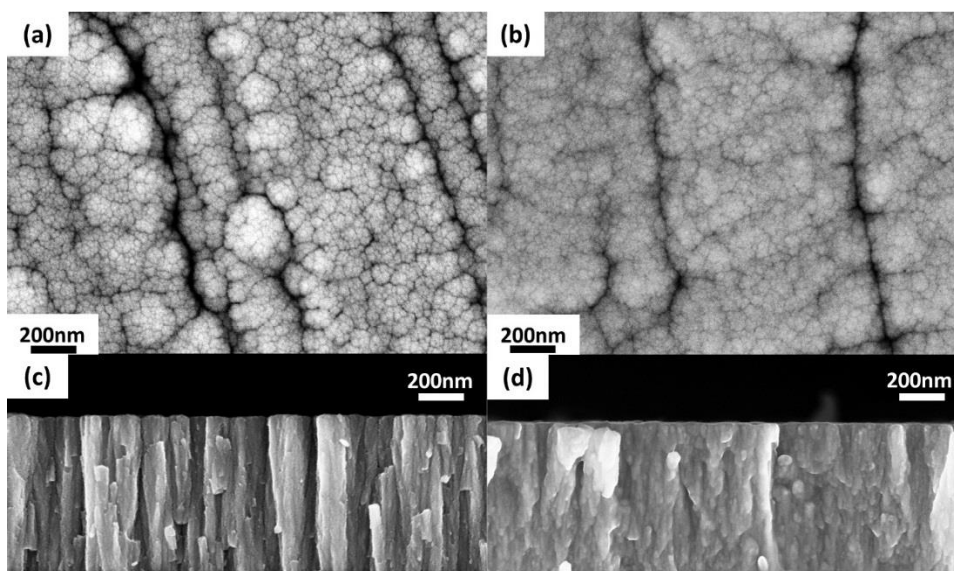


Figure 3.2. SEM plan-view images of coatings of (a) ZrSi_2 deposited at 1.33 Pa Ar gas pressure and (b) ZrSi_2 deposited at 0.53 Pa Ar gas pressure on Zirc-4 substrate. SEM cross-sectional fracture surface images of (c) ZrSi_2 deposited at 1.33 Pa Ar gas pressure and (d) ZrSi_2 deposited at 0.53 Pa Ar gas pressure on a silicon wafer. The dimensional

difference for the microstructure is attributed to nature and roughness of the substrates. The image in Figure 3.2a was from the coating deposited on 600 grit surface finish Zirc-4 substrate while Figure 3.2c is the image of the coating deposited on atomically smooth Si wafers.

Effect of substrate temperature during the sputter deposition on coating quality was briefly investigated. The ZrSi_2 coating deposited at 300 °C showed slightly thicker coating than at room temperature but surface morphology was bulbous in nature typical of sputter coating. Due to concern about thermal stress in the coating during the heating profile, deposition process at higher temperature was excluded from this study.

3.1.2. Structural Phase of As-deposited Coatings

Elemental composition of the very near surface of the as-deposited coatings, as analyzed by the XPS, was consistent in trend with the corresponding target chemistry. Argon gas pressure during the deposition process did not influence the coating composition. Grazing incidence XRD patterns showed only peaks corresponding to zirconium from the underlying substrate and no peaks corresponding to the coatings was observed for any of the coating stoichiometries (Figure 3.3).

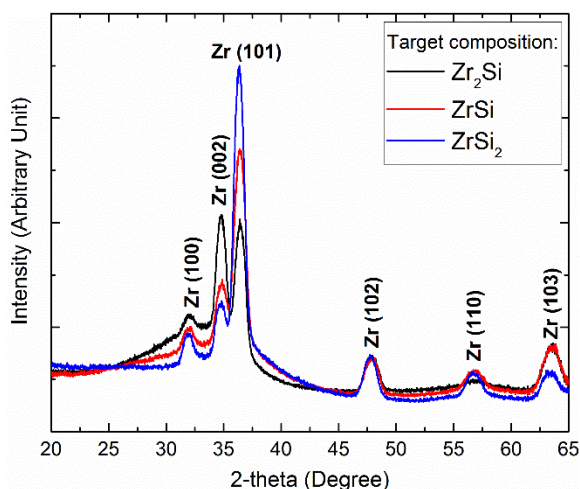


Figure 3.3. XRD patterns of thin coatings (Zr_2Si , ZrSi , and ZrSi_2) deposited at 1.33Pa Ar and 135 W at room temperature for 150 minutes with 2° incident x-ray beam. Only zirconium peaks from the underlying substrate were identified.

The microstructures of the as-deposited coatings were additionally investigated by TEM. The cross-sectional bright field TEM image (Figure 3.4a) for the as-deposited ZrSi_2 (0.53 Pa) coating displayed a columnar structure defined by the voided boundaries aligned with the film growth direction, but no clear contrast was observed between the grains. Selected area diffraction (SAD) pattern (Figure 3.4b) for the corresponding area exhibited diffused halos with fuzzy rings. No distinct diffraction spots characteristic of crystalline phases was observed. Based on XRD patterns and the TEM-SAD analysis, it is speculated that the as-deposited zirconium-silicide coatings are likely amorphous or consist of small volume fraction of nanocrystalline phases in an amorphous matrix. High resolution TEM (HRTEM) images will be required for further analysis of the structure of the as-deposited coatings. The coating composition, phase content, microstructure, and thickness are summarized in Table 3.3.

Table 3.3. Composition, phase content, microstructure, and thickness of the as-deposited coatings.

Target Composition	Ar pressure (Pa)	Temperature (°C)	Coating composition	Major structural phase	Microstructure	Thickness (nm)
Zr_2Si	1.33	19	$\text{Zr}_{2.2}\text{Si}_{1.0}$	Amorphous	Long, tapered, columnar	920
ZrSi	1.33	19	$\text{Zr}_{1.1}\text{Si}_{1.0}$	Amorphous	Long, tapered, columnar	870
ZrSi_2	1.33	19	$\text{Zr}_{1.0}\text{Si}_{1.9}$	Amorphous	Long, tapered, columnar	800

Zr ₂ Si	0.53	19	Zr _{2.2} Si _{1.0}	Amorphous	Short, dense, columnar	800
ZrSi	0.53	19	Zr _{1.0} Si _{1.0}	Amorphous	Short, dense, columnar	750
ZrSi ₂	0.53	19	Zr _{1.0} Si _{2.2}	Amorphous	Short, dense, columnar	720

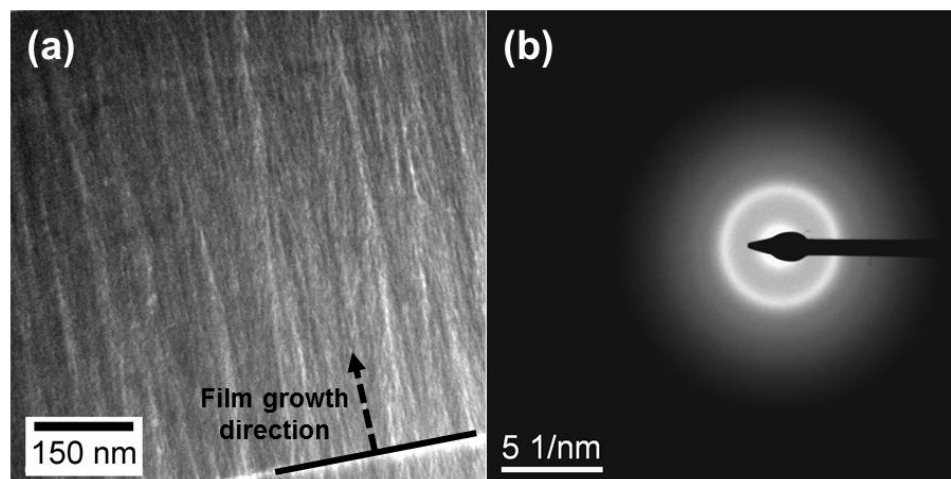


Figure 3.4. (a) Cross-sectional bright field TEM image and (b) diffraction pattern of ZrSi₂ (deposited at 0.53 Pa Ar pressure and room temperature). The coating thickness was 3 μm and was prepared by a four-step deposition for the diffraction pattern observation because an electron beam should illuminate the area of interested through the SAD aperture (1 μm diameter). Coating growth direction is indicated by the black dot arrow.

3.1.4. Compositional Effects on Oxidation

The thin coatings at the lower pressure with three compositions (Zr₂Si #2, ZrSi#2, and ZrSi₂#2) deposited on Zirc-4 coupons were oxidized at 700 °C for 5 hours in ambient air to evaluate their oxidation resistance as a function of coating stoichiometry. Figure 3.5 shows the weight changes (per unit area of the sample) of the coatings of the three stoichiometries and uncoated Zirc-4 at each hour of oxidation. Rapid uptake of oxygen was identified for all the samples during the first hour of exposure, followed by relatively moderate oxidation rate. The formation of passive oxide layer during the initial exposure results in a self-limiting oxidation behavior. All the coatings revealed lower weight gain compared to the bare Zirc-4. In particular, the coating with highest Si content (i.e., ZrSi₂) displayed the lowest weight gain (about 60% compared to the bare Zirc-4). Since only the two major surfaces of the substrates were primarily coated, the weight gain results underestimate the actual improvements in oxidation resistance of the coatings. Therefore, observation of oxide layer thickness by cross-sectional SEM images was deemed to be a more realistic assessment of the improvements in oxidation behavior due to the coatings.

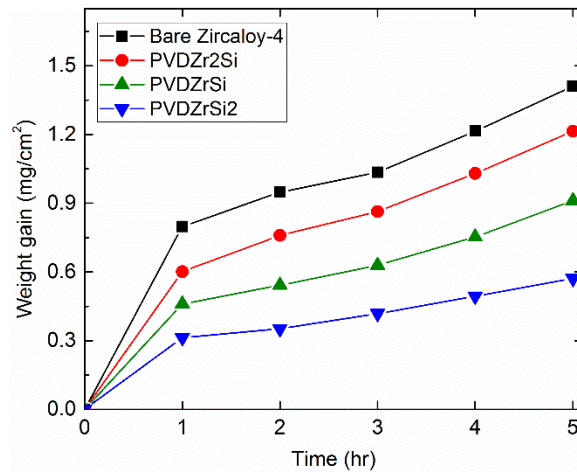


Figure 3.5. Weight gain of the zirconium-silicide coatings with different compositions (Zr_2Si , ZrSi , and ZrSi_2) in 700 °C air oxidation test. The coatings were deposited at 0.53 Pa argon pressure.

The thickness of oxide layer of the coatings was measured by cross-sectional SEM images (Figure 3.6), and the trends were in good agreement with the weight gain results. Significant oxide layer (13-15 μm) developed underneath the Zr_2Si coating due to permeation of oxygen through the coating and its diffusion into the underlying Zirc-4 substrate. The ZrSi coating appeared to form a thinner zirconium oxide in the underlying Zirc-4 alloy substrate. However, no oxide layer was observed in the underlying Zirc-4 alloy substrate for the ZrSi_2 coating. The high magnification images of the oxide scales (Figure 3.6d-f) revealed local variation of composition in the thin coatings and substrate. In the upper region of the Zr_2Si and the ZrSi coatings, zirconium-rich oxide was identified by EDS analysis (the brighter regions in Figure 3.6d-e), which also contained microcracks which would allow for oxygen permeation to the underlying substrate. However, the oxidized ZrSi_2 coating did not show the zirconium-rich oxide in the coating but instead revealed a homogenous microstructure. In addition, for the ZrSi_2 coating, silicon diffusion from the coating to the substrate was clearly detected which may promote coating-substrate adhesion. The Si diffusion depth was about 590 nm, and the composition of this region was predominantly ZrSi .

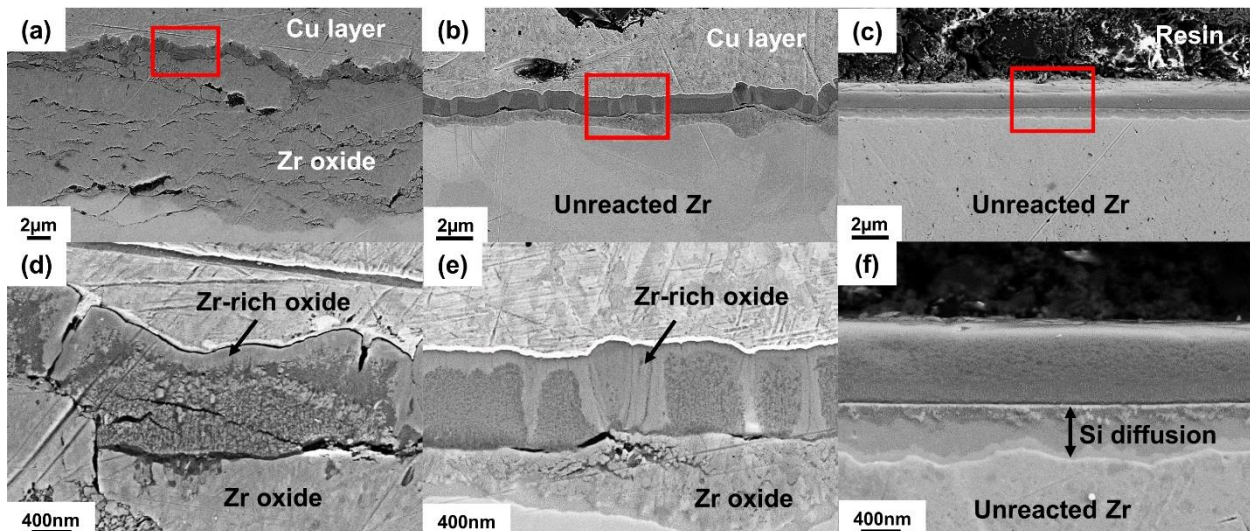


Figure 3.6. SEM cross sectional images of (a, d) Zr_2Si , (b, e) ZrSi , and (c, f) ZrSi_2 coatings at low and high magnifications after 700 °C for 5-hours air oxidation test. The high magnification images were acquired in the areas indicated by the red frames in the low magnification images. Cu layer was deposited on the coating surface by

electroplating to minimize coating damage and edge retention during the sample preparation. All the coatings were deposited at 0.53 Pa argon pressure.

Figure 3.7 shows scratch track (120 ° diamond tip - a standard Rockwell indenter under 250 g applied load) on the coatings after the oxidation test to evaluate adhesion to the substrate and coating cohesion. The cracks and spallation were observed on only the Zr_2Si coatings. It is believed that the damage is attributed to the weak adhesion between the Zr_2Si coating and ZrO_2 scale as shown in Figure 3.6a. However, it was difficult to identify scratch marks and delamination of layers on the ZrSi and ZrSi_2 coating surfaces, indicating a good mechanical robustness of the coatings. It appears that development of ZrO_2 underneath the coatings is related to the mechanical performance, and the results are consistent with the SEM cross-sectional images shown in Figure 3.6.

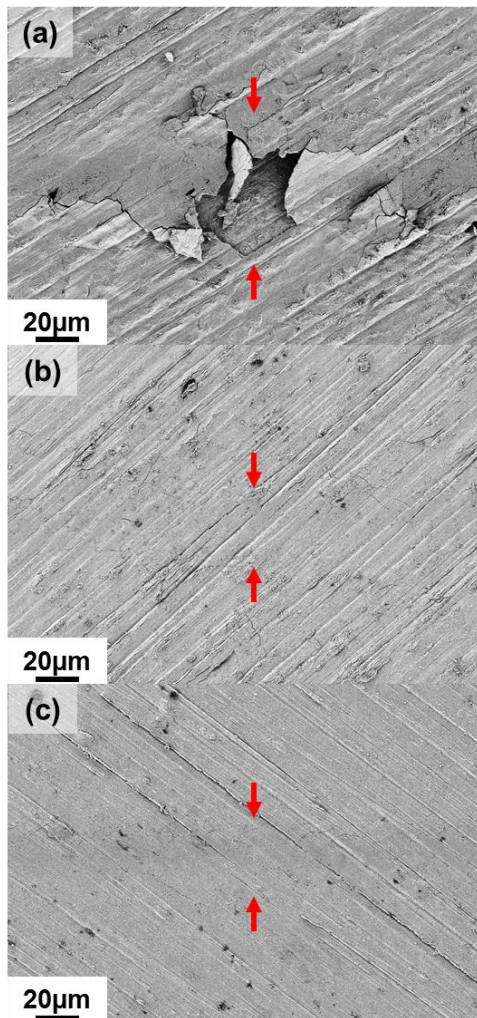


Figure 3.7. SEM plan-view images of oxidized zirconium-silicide coatings (a) Zr_2Si , (b) ZrSi , and (c) ZrSi_2 after the scratch test (250g, applied load). The red arrows indicate scratch tracks.

The near-surface chemical composition and phase evolution of the oxidized coatings was analyzed by XPS (signal acquired over a 400 µm diameter circular region). The binding energy spectrum for O1s in each coating after the oxidation is shown in Figure 3.8. The peak binding energy increased with increasing silicon concentration in the coating, which means that characteristics of chemical bonds associated with oxygen were different depending on coating composition. To provide for a better understanding of the

binding energy shift, deconvolution of O1s binding energy for the oxidized coatings was performed via commercial software (Origin 2015). First, the possible binding energy spectrum was assumed to be from three types of potential oxides with Gaussian distribution. The peak energies of these oxides were taken from literature to be, 531.8 eV (ZrSiO_4) [64], 532.4 eV (SiO_2) [65], and 530.5 eV (ZrO_2) [64,66]. The intensity and FWHM for the components were arbitrarily chosen and iteration using the software was conducted up to the minimum residue between the sum of the estimated oxide spectra and the measured O1s binding energy curve. The deconvolution results indicate the intensity of each oxide component strongly depends on concentration of silicon or zirconium in the coating. The major oxide phase for the zirconium-rich coating (i.e., Zr_2Si) was ZrO_2 with minor ZrSiO_4 but that for the silicon-rich coating (i.e., ZrSi_2) it was SiO_2 with minor ZrSiO_4 . The oxidized ZrSi coating showed strong ZrSiO_4 peak with weak ZrO_2 and SiO_2 peaks. The XPS data for the coatings are in good agreement with the pseudo-binary ZrO_2 - SiO_2 phase diagram [67]. Theoretically, ZrSiO_4 is the only single stable phase in ZrSi oxidation but compositional alteration due to the high mobility of silicon may result in ZrO_2 and SiO_2 formation by modulation of activities of zirconium and silicon. In addition, it is speculated that ZrO_2 formation in the coating is one factor that undermines oxidation resistance of the zirconium-silicide coating at elevated temperatures. The weight gain and oxide layer underneath the coatings are proportional to the intensity of ZrO_2 spectrum in the oxidized coating. This is because of relatively higher oxygen transport rate for ZrO_2 through grain boundaries [68] and crack formation in zirconium-rich oxide. However, very low oxygen permeation in SiO_2 and excellent corrosion resistance of ZrSiO_4 [7] appeared to be very beneficial in preventing oxygen permeation to underlying Zirc-4 alloy substrate in high temperature air environment.

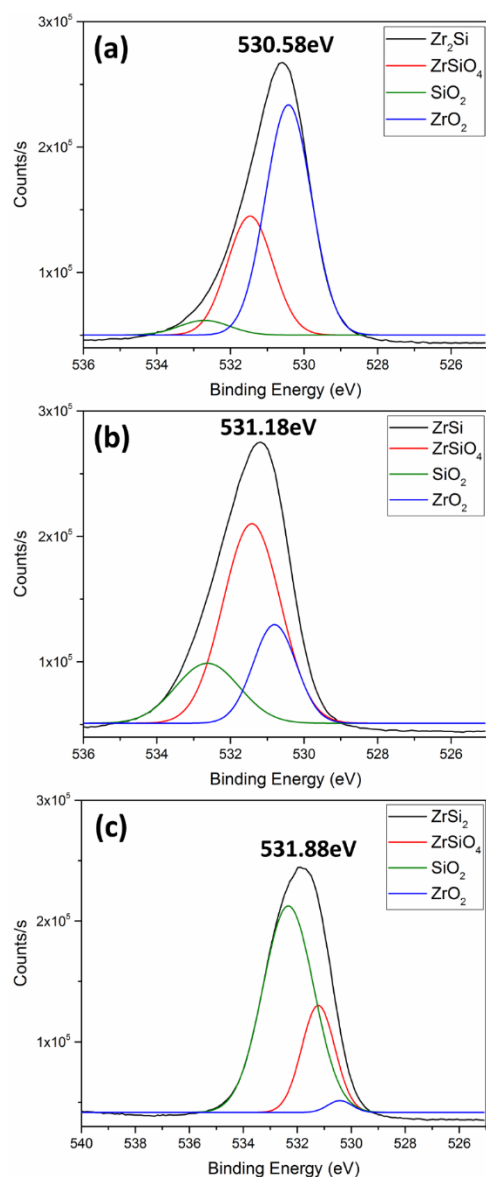


Figure 3.8. XPS O1s spectra of zirconium-silicide coatings after 700 °C for 5-hours oxidation: (a) Zr_2Si , (b) ZrSi , and (c) ZrSi_2 . The O1s spectra were resolved into possible oxide components (red curve: ZrSiO_4 , green curve: SiO_2 , and blue curve: ZrO_2). The measured spectrum is indicated by dark curve. The coatings were deposited on Zirc-4 substrate under 0.53 Pa Ar pressure and room temperature.

3.1.5. Multilayered Zirconium-Silicide Coating

Deposition of multilayered PVD coating with all three aforementioned stoichiometries was performed in order to achieve a compositionally and functionally graded coating with the goal of maximizing coating adhesion to substrate and oxidation resistance. The multilayered coating architecture is as follows: The first layer contacting with the Zirc-4 substrate is Zr_2Si , acting as buffer layer to increase adhesion and the middle layer was ZrSi , and the top layer was ZrSi_2 to achieve oxidation resistance. The multilayered coating was deposited on silicon wafers for a preliminary investigation. The cross-sectional images (Figure 3.9a-b) of the coating deposited on the Si wafer shows that the interfaces between coatings were indistinguishable and

defect free. In addition, elemental concentration of silicon and zirconium at each layer was consistent with the proposed multilayered coating, as confirmed by EDS line scan analysis (Figure 3.9c-d).

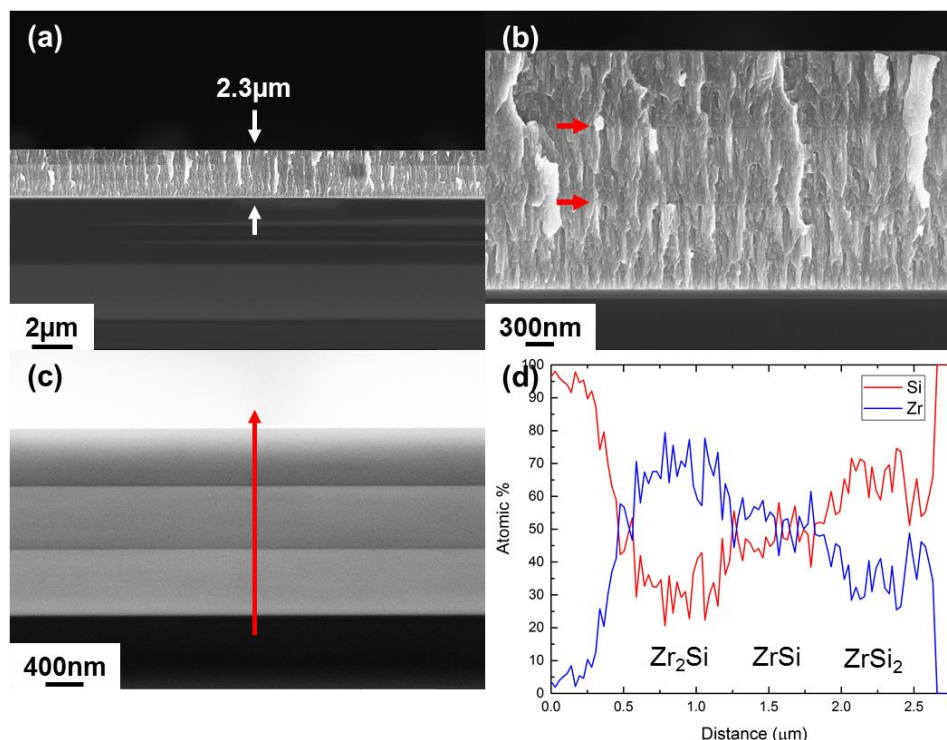


Figure. 3.9. SEM cross-sectional images (5kV) of the multilayered coating on Si wafer at (a) low magnification and (b) high magnification. The red arrows indicate the interface between each compositional layer. (c) SEM image with high voltage (12kV) for EDS line scan and (d) corresponding the EDS line scan result for Si and Zr concentration.

The multilayered coating on Zirc-4 substrate was oxidized at 700 °C for 5 hours in ambient air to demonstrate oxidation resistance of the coatings. The cross-sectional SEM images (Figure 3.10a) showed excellent adhesion of the coating to the Zirc-4 substrate. It appeared that the multilayered coating protected the substrate from the high temperature air. However, the substrate oxidation and cracks were identified in local areas (Figure 3.10b), which may be attributed to a microstructure of the Zr₂Si layer (i.e., dome shape microstructures) acting as a short circuit for oxygen to be permeated. The tapered microstructure in magnetron sputter coating is generally associated with low processing temperature and surface contamination. The results of EDS line-scan reveals that oxygen could not reach the Zirc-4 substrate but significant oxygen concentration was detected in the ZrSi₂ and ZrSi layers. Composition of the coatings in terms of Si and Zr were altered during the oxidation test. Formation of the defect in the coating and thermal stability of the coatings were investigated further by heat treatment in inert gas.

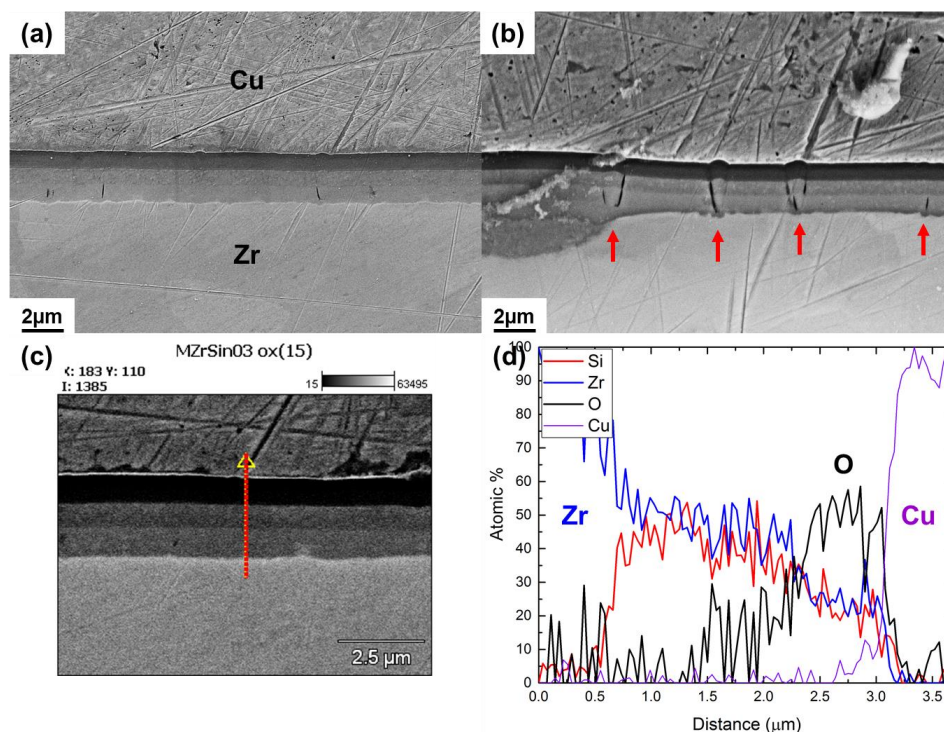


Figure 3.10. SEM cross-sectional images of the multilayered coating on Zirc-4 substrate after exposure at 700 °C for 5 hours: (a) imaged at 3 kV and (b) imaged at 12 kV. The red arrows indicate tapered structures being initiated in the Zr₂Si layer. (c, d) results of EDS line scan in terms of Zr, Si, O, and Cu.

The Zr₂Si coating showed a local variation of composition but reactivity with the substrate was not distinctively identified based on the SEM image and EDS analysis (Figure 3.11a). A decrease in zirconium-to-silicon ratio in the middle of the Zr₂Si coating (indicated by the cross mark in Figure 3.11a) was observed. It is believed that residual oxygen inside the quartz capsule reacted with the surface of the Zr₂Si coating, followed by the formation of Zr-rich oxide on the surface. Thus, silicon atoms on the surface diffused inward and increased the Si concentration however this diffusion was not far enough to reach the substrate. The SEM image of the annealed ZrSi coating displays a thin silicon-rich dark line arising from oxidation-induced silicon diffusion from the surface and silicon diffusion zone in the substrate (Figure 3.11b). It is worth noting that a network of micron-scale cracks in the annealed Zr₂Si and ZrSi coatings was observed as shown in Figure 3.11c. The cracks appeared to initiate from conical-shaped defects which propagated to the substrate. Formation of the defects in Zr₂Si coating was also observed in the multilayered coating at 700 °C. It is expected that oxygen would readily permeate the coating through the open gap around these defects at elevated temperatures, resulting in reduced oxidation resistance. The annealed ZrSi₂ coating showed silicon diffusion to the substrate similar to the oxidized ZrSi₂ coating discussed earlier but the diffusion depth was smaller (~310 nm) than the air-oxidized samples (~590 nm), indicating that surface oxidation also drives Si inward towards to the coating-substrate interface. One plausible explanation is that oxidation generates additional unbound silicon atoms in oxide scale, which is supported by a previous study [69] - bulk ZrSi₂ oxidation at 700 °C in ambient air produced a solid-state mixture Zr-Si-O and a silicon phase. The newly released free silicon atoms showed a high diffusivity, and were associated with evolution of complex microstructures. In addition, XRD analysis for the annealed coatings showed not only strong zirconium peaks from the substrate but also weak zirconium-silicide peaks, indicating initiation of crystallization of the coatings. In summary, the annealing experiments confirmed compositional alteration

of zirconium-silicide coatings (Zr_2Si , ZrSi , and ZrSi_2) on Zirc-4 substrate at 700 °C mainly due to the mobility of silicon atoms in the coatings followed by the reaction with the substrate.

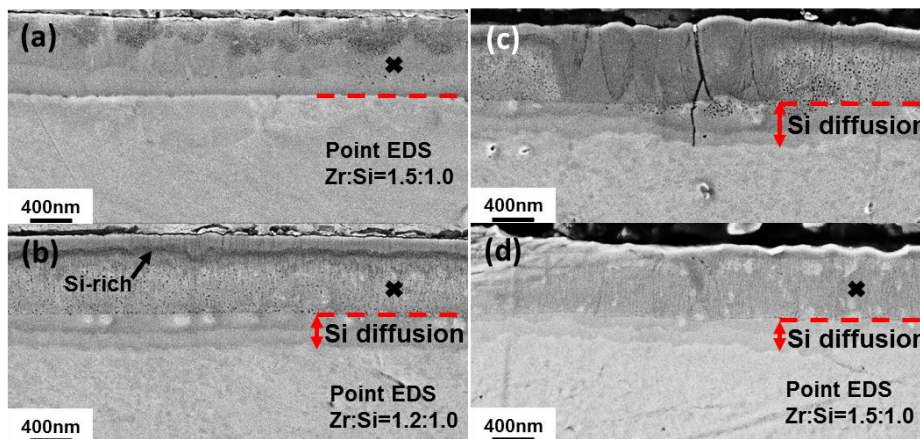


Figure 3.11. SEM cross-sectional images of (a) Zr_2Si , (b, c) ZrSi , and ZrSi_2 annealed at 700 °C for 5 hours in argon gas. Interface between the coating and the substrate and silicon diffused zone are indicated by the red dot line and red arrow, respectively. A ratio of zirconium-to-silicon at the dark cross is stated on each figure as measured by EDS point scan analysis.

3.2. High Temperature Air Oxidation of Coatings

Based on the oxidation and annealing of the zirconium-silicide coatings at 700 °C for 5 hours discussed in the last section, silicon-rich zirconium-silicide stoichiometry, ZrSi_2 , was selected as a potential oxidation resistant coating for Zirc-4. For this next phase of the study, a thicker optimized ZrSi_2 coating was prepared by multiple deposition steps under 0.53 Pa Ar pressure and 19 °C substrate temperature. Plasma cleaning for substrates was performed prior to deposition of the coating.

A cross-sectional SEM in-lens image for the optimized coating is shown in Figure 3.12. The coating thickness was approximately 3.9 μm . The coating displayed dense and columnar microstructure and the interface between each deposition step is revealed as the faint horizontal lines. No spallation or cracks were identified. To evaluate oxidation resistance of the optimized coating, three oxidation experiments were conducted for the ZrSi_2 coating on Zirc-4 flats: 1) 700 °C for 20 hours, 2) 1000 °C for 1 hour, and 3) 1200 °C for 10 minutes. Extremely high temperature oxidation (1400 °C for 5 hours in ambient air) was performed for ZrSi_2 coatings only on SiC flats (as a test for future use of SiC-SiC composite cladding) due to severe degradation of Zirc-4 substrate at this high temperature.

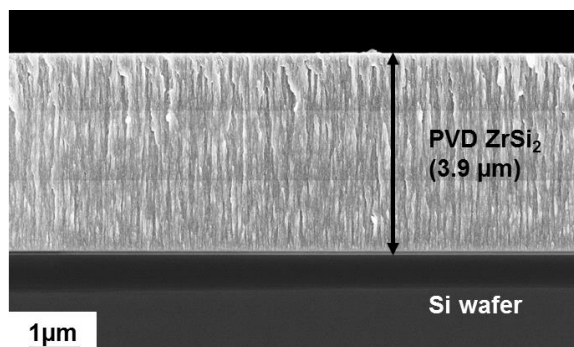


Figure 3.12. SEM cross-sectional image of as-deposited ZrSi_2 coating on silicon wafer for the 700 °C, 1000 °C, and 1200 °C oxidation tests.

3.2.1. Oxidation of Optimized ZrSi₂ Coating at 700 °C

The longer oxidation for the coating at 700 °C enabled us to better understand oxide scale growth on the coating and phase stability in the coating/substrate interface. The samples were heated up to 700 °C with slow ramp rate (5 °C/min) and then held at this temperature for 20 hours, followed by air cooling. As shown in Figure 3.12a, oxygen permeation through the coating was very low and the thin oxide layer of thickness of only about 750 nm formed on the top surface of the coating during the 20-hour oxidation. In contrast, the bare Zirc-4 substrate developed about a 65 µm thick oxide layer. This suggests that oxidation resistance factor of improvement of the coating is more than 85 compared to bare Zirc-4 at 700 °C air. The very near-surface atomic percent of the oxide layer was 14%-Zr, 19%-Si, and 66%-O as measured by XPS (Table 3.4) and corresponding binding energy spectra are identical to those of the thin ZrSi₂ layer after the 700 °C for 5-hours air oxidation. The protective nature of the coating is mainly attributed by the SiO₂ and ZrSiO₄ oxide layer.

The XRD pattern (Figure 3.12b) revealed not only ZrSi₂ arising from crystallization of the unreacted coating and zirconium substrate peaks, but also a broad halo in the range of 24° to 30° in 2θ. Possible phases associated with the broad hump are ZrSi₂, SiO₂ (quartz), and ZrSiO₄ listed as follows: ZrSi₂ (040) at 24.05°, ZrSi₂ (021) at 24.79°, ZrSi₂ (130) at 30.19°, SiO₂ (011) at 25.16°, SiO₂ (220) at 28.41°, SiO₂ (310) at 28.48°, and ZrSiO₄ (200) at 26.67°. The XRD pattern could be a superposition of the nanocrystalline phases and amorphous phase, assuming that nanocrystalline phases (ZrSiO₂, SiO₂, and ZrSi₂) were precipitating in amorphous oxide matrix during the 700 °C oxidation. The phases constituting the thin protective oxide layer is also consistent with an oxide layer formed on bulk ZrSi₂ in 700 °C in ambient air. In addition, the silicon diffusion zone into the Zirc-4 alloy of thickness of 630 nm was identified. Interestingly, the silicon atoms were supplied from about 1.4 µm of the ZrSi₂ coating contacting with the substrate because the region displayed silicon reduction (ZrSi₂ → ZrSi_{1.5}) and formation of nano-scale pores due to clustering of vacancies from the substitutional diffusion of Si (dark spots in Figure 3.12a).

Table 3.4. XPS compositional analysis of the optimized coatings (ZrSi₂) after the oxidation tests. The numbers are in atomic percent of each element on the very near-surface. The last column shows the atomic percent ratio of zirconium and silicon.

Oxidation Test	Si2p	Zr3d	O1s	C1s	Zr : Si
700 °C for 20 hours	18.82	13.63	65.50	2.06	1.0:1.4
1000 °C for 1 hour	15.06	17.88	64.78	1.67	1.2:1.0
700 °C for 5 hours → 1000 °C for 1 hour	17.24	14.40	67.07	1.30	1.0:1.2
700 °C for 5 hours → 1200 °C for 10 minutes	15.99	15.10	67.68	1.23	1.0:1.1

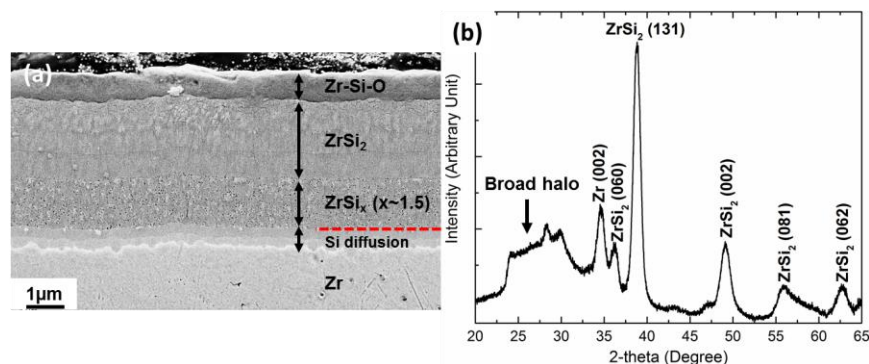


Figure 3.12. SEM cross-sectional image of (a) oxidized ZrSi₂ coating on Zirc-4 at 700 °C for 20 hours. Interface between the coating and the substrate is indicated by the red dots. (b) XRD pattern for the oxidized ZrSi₂ on Zirc-4 at 700 °C for 20 hours. The dark arrow in Figure 3.12b points to broad halo (or hump) associating with the thin oxide layer in Figure 3.12a.

3.2.2. Oxidation of Optimized ZrSi_2 Coating at 1000 °C and 1200 °C

The high temperature oxidation tests for the optimized coatings were conducted at 1000 °C for 1 hour and 1200 °C for 10 minutes. For these tests, the coated samples were inserted directly in a pre-heated furnace resulting in a rapid heating rate. After the exposure, the samples were air-cooled to room temperature. These tests demonstrated material degradation due to oxidation and thermal shock. For these tests, two types of samples were evaluated, (i) as-deposited coating and (ii) after pre-oxidation at 700 °C air for 5 hours. The pre-oxidation condition was the same as was used for the oxidation tests for thin coatings discussed earlier. Thus, the pre-oxidized samples used for the 1000 °C and 1200 °C would have the same submicron thickness protective oxide layer. As shown in Figure 3.13a-b, significant differences in surface morphology between the as-deposited coating and the pre-oxidized coating were observed after the 1000 °C oxidation. Micron-scale cracks were observed (Figure 3.13a) on the entire area of the as-deposited coating, indicating the coating did not provide the necessary oxidation resistance. The degradation of the as-deposited coating might be explained by the absence of the protective oxide layer and loss of thermal stability of the coating. A sudden temperature surge to 1000 °C in air produced ZrO_2 on the surface due to silicon inward diffusion rather than formation of the Zr-Si-O protective oxide layer. As discussed in the previous section, silicon diffusion from the ZrSi_2 coating to Zirc-4 substrate was identified at 700 °C in both oxidation and annealing. Increase in Zr-to-Si ratio on the oxidized surface at 1000 °C without the pre-oxidation as confirmed in the XPS analysis, and the local silicon rich area in the cross-sectional image of the coating (Figure 3.13c) also support this explanation. According to the diffusion couple experiments between Ti_3SiC_2 and Zirc-4 [48], the effective diffusion coefficient of Si in Zirc-4 at 1300 °C was approximately six times larger than that at 1100 °C. Therefore, remarkably rapid silicon loss in the coating, which accelerated by the surface oxidation at 1000 °C in the absence of the protective layer, generated microstructural defects (i.e., clusters of voids) in the coating, which in turn induced the crack formation and intensified material degradation. On the other hand, not only no noticeable defects such as delamination, cracks, or spallation but also higher silicon concentration compared to zirconium on the very near-surface was observed on the pre-oxidized coating surfaces with the 1000 °C and 1200 °C exposures.

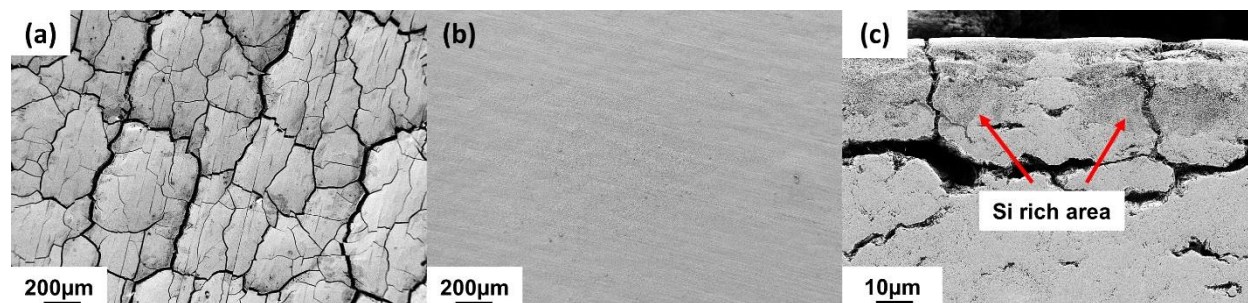


Figure 3.13. SEM plan-view images of (a) ZrSi_2 oxidized at 1000 °C for 1 hour, (b) ZrSi_2 with pre-oxidation (700 °C for 5 hours) oxidized at 1000 °C for 1 hour, and (c) cross-sectional image of ZrSi_2 with pre-oxidation (700 °C for 5 hours) oxidized at 1000 °C for 1 hour, showing cracks and Si rich area in the thick oxide scale. The samples were rapidly heated up to the high temperature air. After the exposure, the coating was air-cooled to room temperature.

The protective nature of the top oxide layer formed on the pre-oxidized sample was also confirmed in the cross-sectional SEM image of the sample after the 1000 °C and 1200 °C oxidation tests (Figure 3.14). After oxidation at 700 °C for 5 hours followed by the 1000 °C for 1 hour, total thickness of the oxide scale for the coating was about 7 μm , but that of the bare Zirc-4 oxidized at the same condition was about 89 μm . However, the as-deposited coating (i.e., without pre-oxidation) after the test had thicker oxide scale (approximately 106 μm) than the bare Zirc-4, possibly resulting from oxygen ingress through the cracks as observed in Figure 3.13a-c. The oxygen penetration depth for the pre-oxidized coating after the 1000 °C test was also measured by EDS line scan analysis as shown in Figure 3.14b. The pre-conditioning produced

about 730 nm thickness oxide layer on the top, ZrO_2 ($\sim 6.3 \mu\text{m}$), ZrSi_2 ($\sim 0.9 \mu\text{m}$), and ZrSi layer ($\sim 3.5 \mu\text{m}$) subsequently. In addition, the oxide layer thickness of the pre-oxidized coating after the 1200 °C test was about 20 μm , which was nearly one-tenth of oxide scale thickness of the bare Zirc-4 (about 208 μm) at this test condition. The oxide scale for the coated samples consisted of thin protective layer (750 nm) on the top, thick ZrO_2 layer ($\sim 17 \mu\text{m}$), ZrSi_2 islands, and ZrSi layer ($\sim 2.3 \mu\text{m}$). Interestingly, the protective oxide layer formed on the pre-oxidation (700 °C) transformed to nanoscale ZrO_2 phase particulates in a SiO_2 matrix at the 1000 °C and 1200 °C exposures as shown in Figure 3.14c-d. The microstructure was not identified in the oxide scale at 700 °C.

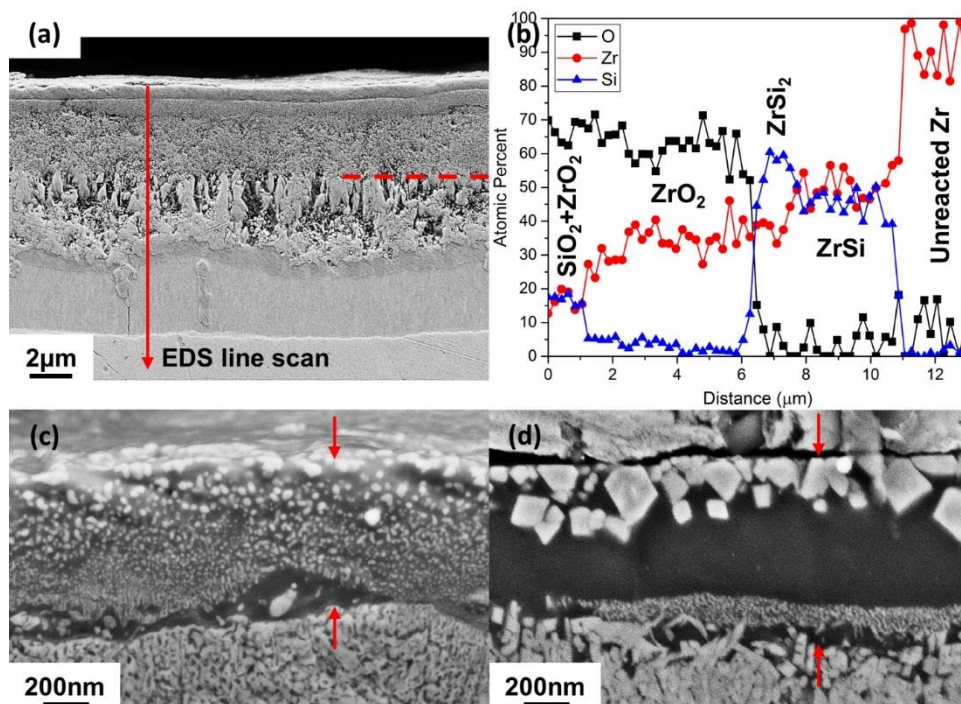


Figure 3.14. SEM cross-sectional images and EDS line scan of ZrSi_2 with the pre-oxidation (700 °C for 5 hours) after the 1000 °C for 1-hour air oxidation: (a) Low magnification and (b) EDS line scan result. The red dots and the solid red arrow in Figure 3.14a refer to interface between the coating and substrate and the EDS scan direction, respectively. High magnification cross-sectional SEM images of top surface of the pre-oxidized coatings after (c) the 1000 °C for 1 hour and (d) the 1200 °C for 10 minutes. The red solid arrows in Figure 3.14c-d refer to the thin protective layer consisting of nanoscale ZrO_2 phases in SiO_2 matrix.

The phase transformation from the Zr-Si-O oxide mixture to the ZrO_2 and SiO_2 phase was also reported in annealing of mixture of ZrO_2 and SiO_2 thin film at 900 °C for 60 seconds [46] and oxidation of bulk ZrSi_2 at 1000 °C and 1200 °C for 5 hours in ambient air. The authors suggested that a thermodynamic driving force exists in disordered Zr-Si-O mixture, leading to nucleation and growth of ZrO_2 in SiO_2 matrix instead of formation of ZrSiO_4 . During the pre-conditioning, the oxide layer consisting of a mixture of nanocrystalline phases and amorphous phase forms, which might heal inherent microstructural defects (i.e., conical defects) so that the oxide layer hindered oxygen permeation during the 1000 °C and 1200 °C oxidation. In addition, the multi-layered scale structure at the high temperatures evolves due to slow oxidation kinetics arising from the thin protective layer. The partial pressure for oxygen might be significantly decreased in the protective layer, resulting in a slower oxidation process of the rest of the ZrSi_2 coating. In the meantime, the silicon in the coating migrates inward to the substrate, increasing activity of zirconium in the outer regions. The mobile silicon atoms reacted with the substrate and formed the ZrSi_2 and ZrSi layers, which is supported by the zirconium-silicon diffusion couple experiments at 900 °C to

1400 °C in inert environments [70]. Hence, as expected, when oxygen diffused through the protective layer and reacted with zirconium atoms, the ZrO_2 scale formed. Lastly, it is expected that oxidation of the ZrSi_2 coating by a pre-oxidation step at even higher temperatures (e.g., 1300 °C or 1400 °C) produces micron-grained ZrSiO_4 phase in the protective layer by solid state reaction of the ZrO_2 particulates and the SiO_2 matrix, which would provide enhanced oxidation resistance.

3.2.3. Oxidation of Optimized ZrSi_2 Coating at 1400 °C

To understand oxidation performance of the ZrSi_2 coatings at extremely high temperatures, the coatings deposited on the two major surfaces of Zirc-4 flats were oxidized at 1400 °C for 5 hours in ambient air. The ramp rate for the oxidation process was 5 °C/min. As shown in Figure 3.15a, the samples were excessively oxidized and crumbled after the oxidation due to oxygen ingress through the uncoated areas (e.g., side areas of the samples). To avoid the substrate effect, commercially available Moissanite 3C (β) – CVD SiC flats were procured and polished progressively with 600 grit SiC abrasive paper followed by cleaning with acetone and methanol. ZrSi_2 coatings of 3 μm thickness of were deposited on one side of these SiC flats using the same magnetron sputter technique. The coated SiC flats were oxidized at 1400 °C for 5 hours in ambient air, and Figure 3.15b shows the oxidized ZrSi_2 coating on SiC samples with the light grey color. No noticeable spallation of the coatings was not observed by the visual inspection.

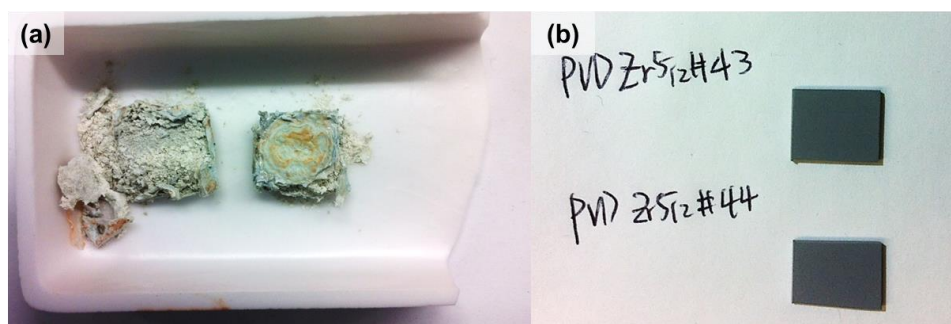


Figure 3.15. Photograph of (a) oxidized ZrSi_2 coatings on Zirc-4 flats and (b) oxidized ZrSi_2 coatings on SiC flats at 1400 C for 5 hours in ambient air.

Figure 3.16 shows SEM plan-view images for bare SiC, as-deposited ZrSi_2 and oxidized ZrSi_2 at 1400 °C. Elemental compositions for the surfaces were also specified on the images. Due to the high hardness of SiC, it was difficult to make the surface smooth and the bare SiC appears to be rough as shown in Figure 3.16a. Nevertheless, the surface ZrSi_2 coating fully covered and filled the pockets on the surface, smoothening the surface as confirmed in Figure 3.16b. The coating surface did not reveal any cracks and delamination after the 1400 °C oxidation test but nano-scale surface structures were identified in the high magnification image (Figure 3.16d), and similar concentration of Zr and Si on the surface is an indicative of formation of ZrSiO_4 phase.

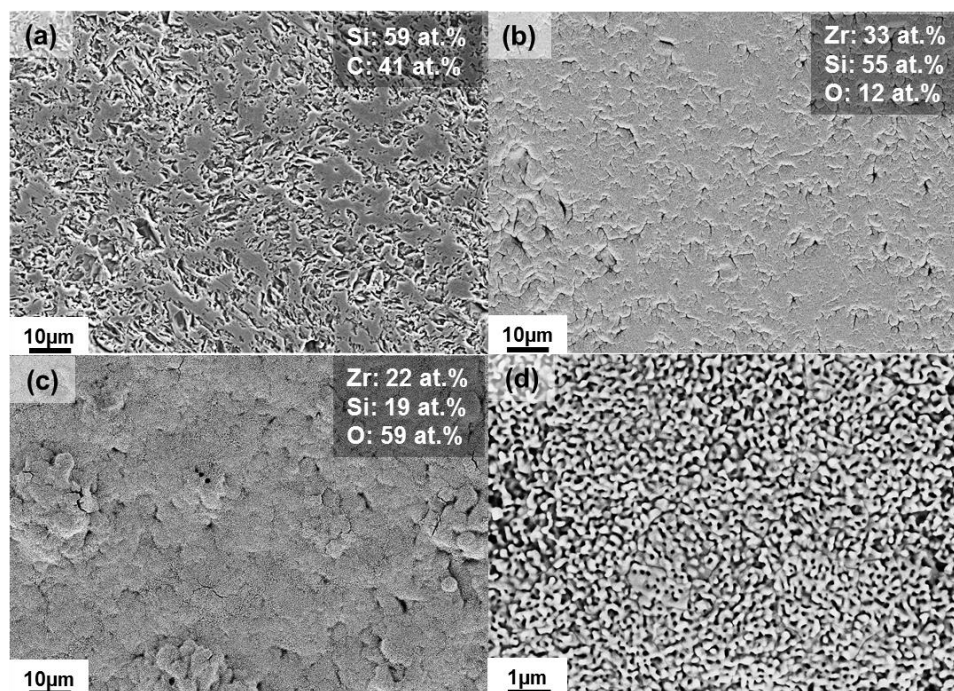


Figure 3.16. SEM plan-view images of (a) bare SiC sample, (b) as-deposited ZrSi_2 coating on SiC and (c) and (d) as-deposited ZrSi_2 coating on SiC after oxidation at low magnification and high magnification, respectively. The insets show area-average EDS results on each surface. The oxidation test was performed at 1400 °C for 5 hours in ambient air.

XRD patterns for the oxidized ZrSi_2 coating are shown in Figure 3.17. The strong zircon peaks, SiC peaks, weak ZrSi_2 peaks, and SiO_2 peaks were identified. It is worth noting that ZrSi_2 coating could produce zircon phase during high temperature oxidation and has the potential to drastically mitigate oxidation given that just underneath the zircon layer unreacted ZrSi_2 phase is still detected after the high temperature oxidation. The SiC of course peaks come from the substrate.

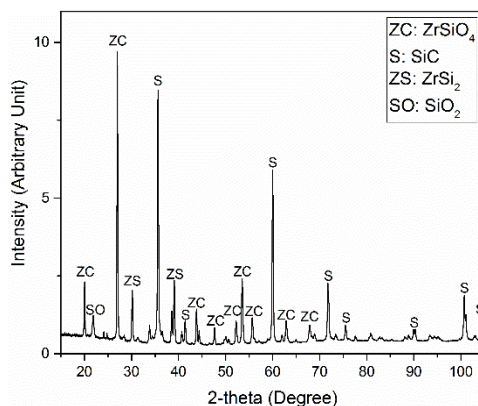


Figure 3.17. XRD pattern for oxidized ZrSi_2 coating on SiC after exposure at 1400 °C for 5 hours in ambient air.

Microstructure of the oxidized ZrSi_2 coating was characterized by SEM cross-sectional imaging as shown in Figure 3.18. The oxide scale for the coating consisted of continuous zircon layer with thickness of approximately 1.9 μm , SiO_2 layer, and islands of unreacted ZrSi_2 . The thickness of the oxide scale was doubled ($\sim 5.4 \mu\text{m}$) compared to the as-deposited coating ($\sim 3 \mu\text{m}$). This is because the volume of the coating

increased during the oxidation process which produces ZrSiO_4 and SiO_2 . Additionally, silicon diffusion to SiC substrate was not identified, a difference from the oxidation for similar coatings on Zirc-4 substrate discussed earlier. It is speculated that top region of the coating reacted with oxygen followed by formation of ZrO_2 , SiO_2 , corresponding to the microstructure of oxide scale for the 1000 °C and 1200 °C oxidation. And then, solid state reaction of the ZrO_2 phases and the SiO_2 produced ZrSiO_4 layer. The inwardly diffusing free Si then oxidizes, resulting in the SiO_2 layer. Due to the excellent oxidation resistance of ZrSiO_4 and SiO_2 layers, unreacted ZrSi_2 islands were observed in the oxide scale. It appears that the SiC substrate remains unreacted because of very low partial pressure of oxygen at the interface. The zircon phases had columnar structures with nano-sized ZrO_2 and SiO_2 phases based on the contrast difference in Figure 3.18b. It is assumed that the dark spots and the bright circles in the zircon layer were SiO_2 and ZrO_2 phases, respectively. The EDS line scan of the cross-sectional image of the oxide scale (Figure 3.19a) was performed and the results are plotted in Figure 3.19b. The compositional plot shows that diffusion of oxygen was effectively mitigated by the ZrSiO_4 and SiO_2 layers.

It is well-known that fabrication of zircon coating is a very difficult process. For example, thermal spray for this material is limited due to phase decomposition of zircon during melting the feed powders above 1670 °C [71,72], and formation of micron-scale thickness of zircon layer takes very long time via atomic layer deposition because of a low yield rate. Moreover, crystalline zircon layer would not be achieved via plasma enhanced chemical vapor deposition at relatively low temperature due to spinodal phase decomposition [45,46]. In the previous sections, performance of the zircon layer at the oxidation/corrosion environments was demonstrated. For instance, the oxide scale of bulk ZrSi_2 at 1400 °C air was thinner than that at 1200 °C air due to formation of zircon surface layer. Under the high temperature steam environment, the immobilization of Si by zircon phase imparted corrosion stability to the material. It is anticipated that the thin and continuous zircon layer on the SiC substrate, produced by the high temperature oxidation of ZrSi_2 coating, might mitigate potential degradation of SiC in higher temperature and water/steam conditions.

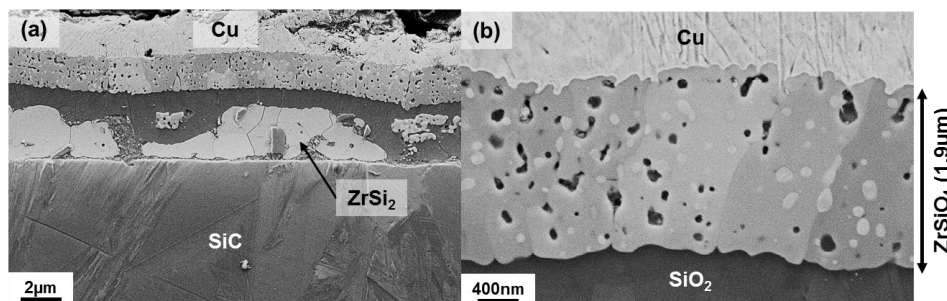


Figure 3.18. SEM cross-sectional images of oxidized ZrSi_2 coating on SiC substrate at 1400 °C for 5 hours in ambient air with (a) low and (b) high magnification.

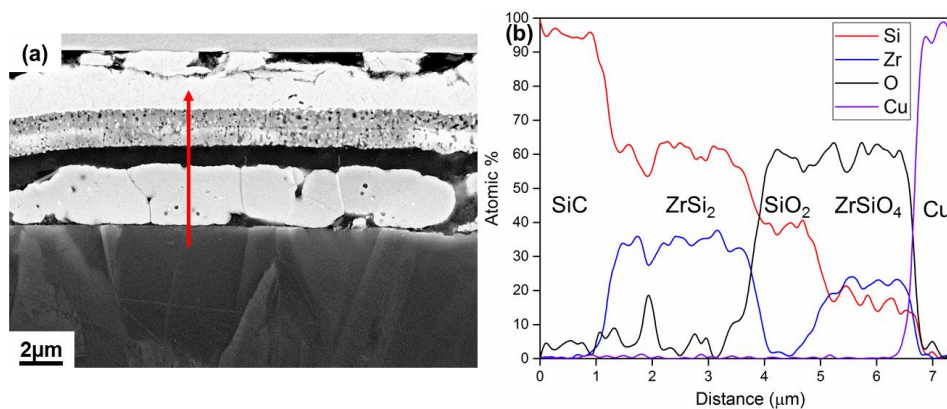


Figure. 3.19. (a) Cross-sectional image of oxidized ZrSi_2 coating on SiC for EDS line scan analysis. The red arrow indicates a path of data collections and (b) the results for Si, Zr, O, and Cu are plotted. The Cu signal was detected from Cu plated layer prepared during a sample preparation.

3.3. Pressurized Steam Corrosion of Coatings

In the last section (Section 3.2), parametric investigations for optimized ZrSi_2 coating were performed, and the oxidation tests examined protective-nature of the optimized coating at elevated temperatures in ambient air. In addition, it was found that zircon (ZrSiO_4) phase was generated during air oxidation of ZrSi_2 coating in 1400 °C air environment. Given the outstanding corrosion resistance of zircon, it was anticipated that it provides corrosion resistance for SiC substrate, which is known to experience silicon depletion in high temperature water/steam environment. In this section, initial evaluation of corrosion resistance of the zirconium-silicide coatings under high temperature water conditions were conducted. ZrSi_2 was first deposited on one surface of Zirc-4 and CVD SiC test flats. After the steam corrosion test, the coatings were characterized by SEM-EDS analysis to quantify any alterations in surface morphology and composition, and thickness of oxide scale. The steam test conditions were identical to the experiments for bulk materials as discussed in Section 2.2. The coated samples were exposed to 400 °C, pure steam (18 MΩ), and 10.3 MPa for 72 hours.

3.3.1. Steam Corrosion Tests of Zr-Si Coatings

Based on the results of optimization process for zirconium-silicide coatings to maximize oxidation resistance under high temperature air, silicon-rich silicide (ZrSi_2) coatings with thickness of 3.9 μm were deposited for the steam corrosion test. Pre-oxidation of the ZrSi_2 coating was performed at 700 °C air for 5 hours prior to the steam test in order to attain the thin oxide layer that showed excellent oxidation resistance in high temperature air environment. To mitigate silicon loss in ZrSi_2 in steam environment several coating system designs were investigated. First, a double-layered Zr-Si coating was investigated – here the inner layer was ZrSi_2 coating for oxidation resistance at high temperatures and outer layer was Zr_2Si coating as a potential water corrosion resistance barrier at high temperature steam environment. In the second approach, some of the double-layered coatings were oxidized at 400 °C air for 10 hours to facilitate formation of Zr-rich oxide on the top surface. Finally, the zircon formed ZrSi_2 coatings, prepared by the 1400 °C air oxidation, were exposed to the steam conditions and surface corrosion of the coatings was observed. The coating designs for steam corrosion test is summarized in Table 3.5.

Table 3.5. Composition, coating thickness, coating substrate, and heat treatment conditions of zirconium-silicide coatings for steam corrosion experiment (400 °C pure steam and 10.3 MPa for 72 hours).

Coating ID	Composition [thickness]	Substrate	Heat Treatment in Air
Zirc-4	Zirconium alloy	Zircaloy-4	None
ZrSi#1	ZrSi_2 [3.9 μm]	Zircaloy-4	None
ZrSi#2	ZrSi_2 [3.9 μm]	Zircaloy-4	700 °C for 5 hours
ZrSi#3	Outer Zr_2Si [3 μm] + Inner ZrSi_2 [3 μm]	Zircaloy-4	None
ZrSi#4	Outer Zr_2Si [3 μm] + Inner ZrSi_2 [3 μm]	Zircaloy-4	400 °C for 10 hours
ZrSi#5	ZrSi_2 [3 μm]	SiC	1400 °C for 5 hours

The double-layered Zr-Si coatings (ZrSi#3) was fabricated by four deposition steps on Zirc-4 flats and Si wafer. The contrast between the two zirconium-silicide layers of different stoichiometries is revealed clearly in SEM cross-sectional image (Figure 3.20a) of the double layered coating system. The brighter area contains more zirconium and less silicon, which is Zr_2Si layer. The columnar microstructures were continuous across the compositional boundary so that excellent adhesion between each layer is expected. The EDS line scan data (Figure 3.20b) confirms again that the double-layered coating consists of Zr_2Si (3 μm in thickness) and ZrSi_2 (3 μm).

Pre-oxidation of the double-layered coatings at 400 °C air for 10 hours facilitated ZrO_2 formation on the surface. Visual inspection showed that the surface color of the coating changed from the original metallic grey to blue. EDS elemental analysis on top of the coating showed an increase in oxygen concentration to 40 at. % but there was no emergence of peaks associated with the formation of crystalline phases (the only peaks were from Zr from the substrate).

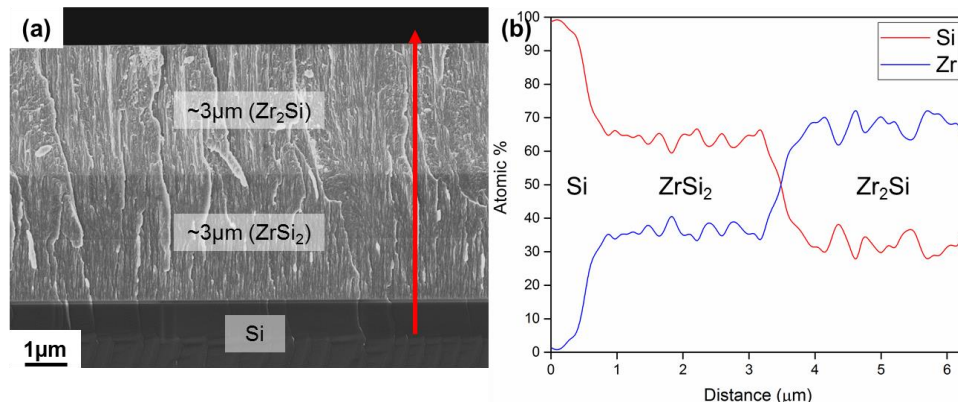


Figure 3.20. (a) SEM cross-sectional image of the double-layered Zr-Si coating on Si wafer and (b) EDS line scan result corresponding to the red arrow.

3.3.2. Steam Corrosion of Optimized ZrSi_2 and Multilayered Coatings

Figure 3.21 shows the surface morphology and elemental composition for the as-deposited ZrSi_2 (ZrSi#1), the pre-oxidized ZrSi_2 (ZrSi#2), and the pre-oxidized double-layered coating (ZrSi#4) after the steam corrosion test. The surface of all the steam autoclave tested Zr-Si coatings showed an increase in oxygen concentration and depletion of silicon atomic percent, and surface cracking. The lesser surface cracks on the ZrSi#1 (Figure 3.21a) compared to the bulk ZrSi_2 (Section 2.2) indicates that the micron sized silicon particulates embedded in the ZrSi_2 matrix weakened mechanical integrity of oxide scale during the steam corrosion. The high magnification SEM images (Figure 3.21b, d, and f) reveal alterations in surface morphology. Due to the reaction with steam, the typical bulbous surface structure of the as-deposited coating changed to the sponge-like surface as shown in Figure 3.21b. The major phase of the porous structure was zirconium-rich oxide. The pre-oxidized ZrSi_2 (ZrSi#2) and the double-layered coatings (ZrSi#3 and ZrSi#4) show coarser and denser porous structure than the as-deposited coating (ZrSi#1), associated with higher activity of zirconium on the surface than silicon while the steam reacted with the coating surface. Nevertheless, existence of the porosity of the surface layer contributed to local cracking, resulting in steam permeation and corrosion.

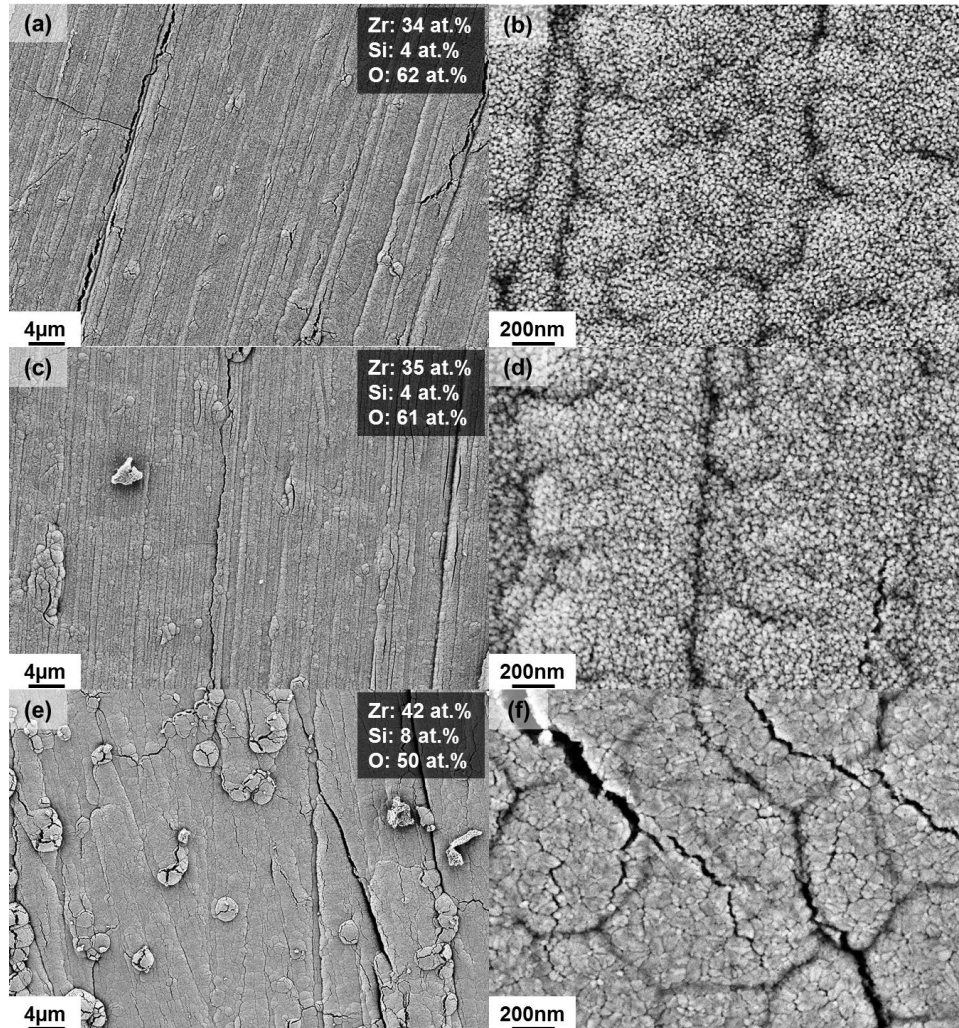


Figure 3.21. SEM plan view images of zirconium-silicide coatings on Zirc-4 and results of EDS analysis after the steam autoclave test: (a, b) as-deposited ZrSi_2 coating (ZrSi#1) at low and high magnifications, (c, d) pre-oxidized ZrSi_2 coating (ZrSi#2) at low and high magnifications, and (e, f) pre-oxidized double-layered coating (ZrSi#4) with magnification.

Cross-sectional SEM images of bare Zirc-4 and zirconium-silicide coatings corroded for 72 hours in autoclave are shown in Figure 3.22. Oxide layer developed on bare Zirc-4 has a thickness of approximately 1.6 μm , and this is consistent with other experimental data for zirconium-alloys after steam corrosion test at 415 $^{\circ}\text{C}$ and 10.5 MPa for 3 days [73,74]. All zirconium-silicide coatings reacted with steam and produced the thick Zr-rich oxide layer with depletion of silicon species. The oxide scale for the pre-oxidized ZrSi_2 coatings (ZrSi#2) was so weak that the Si-depletion layer was damaged and removed during sample preparation for the SEM imaging. Therefore, it is not shown in Figure 3.22c. The images reveal that the ZrSi_2 coatings (ZrSi#1 and ZrSi#2) prevented oxide formation at the Zirc-4 interface. After the autoclave test, thickness of the uncorroded coating for ZrSi#2 is thicker than that of ZrSi#1. It is speculated that the thin oxide layer formed at 700 $^{\circ}\text{C}$ air is beneficial to mitigating the kinetics of the reaction between ZrSi_2 and steam. The amorphous-nanocrystalline phase of the oxide scale might act as a diffusion barrier even if the oxide layer containing SiO_2 is removed by dissolution or volatilization in the steam environment. Moreover, the remaining ZrSi_2 coating in ZrSi#2 after the test is confirmed in EDS elemental mapping as

shown in Figure 3.23. Small portion of the coating (approximately 0.6 μm) disappeared during the steam corrosion (and a lesser degree during sample preparation) but the rest of the coating was intact, as indicated by a pronounced silicon signal in absence of oxygen in the EDS map. However, the double-layered coatings (ZrSi#3 and ZrSi#4) were fully oxidized and even a thin oxide scale on Zirc-4 substrate was identified. It appears that there was no positive contribution of the Zr_2Si coating to corrosion resistance. Furthermore, the Zr_2Si coating might accelerate corrosion of the underneath ZrSi_2 layer because of evolution of micro-cracks, resulting in oxidation of Zirc-4 substrate. The detrimental effect could be associated with the conical microstructures in Zr_2Si and thermal expansion mismatch in the compositional interface.

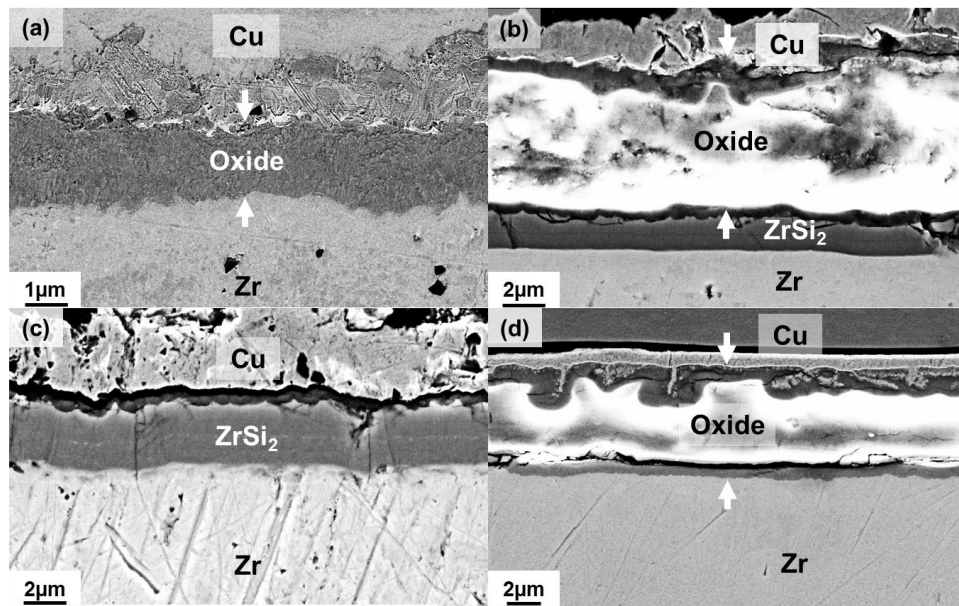


Figure 3.22. SEM cross-sectional images of (a) bare Zirc-4, (b) as-deposited ZrSi_2 (ZrSi#1), (c) pre-oxidized ZrSi_2 at 700 °C (ZrSi#2), and (d) pre-oxidized double-layered coating (ZrSi#4) after the steam corrosion test. Cu plating was performed on the corroded surfaces as a surface protection. The white arrows indicate the oxide scales.

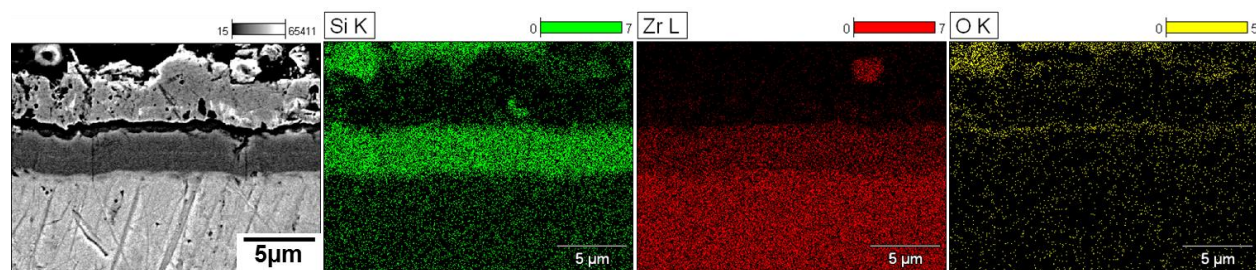


Figure 3.23. EDS spectra mapping of the pre-oxidized ZrSi_2 at 700 °C (ZrSi#2) after the steam corrosion test, showing unreacted ZrSi_2 coating on Zirc-4 substrate.

Table 3.6 provides a summary of performance of the zirconium-silicide coatings under the high temperature steam conditions. It is evident that ZrSi_2 coating with the pre-oxidation (700 °C air for 5 hours) provides the best corrosion resistance for Zirc-4 substrate among the Zr-Si coatings.

Table 3.6. Summary of corrosion of the zirconium-silicide coatings under 400 °C and 10.3 MPa steam for 72 hours.

Coating ID	Composition [thickness]	Remained Coating (μm)	Substrate Oxidation (μm)
Zirc-4	Zirconium alloy	N/A	1.6 – 2.2
ZrSi#1	ZrSi_2 [3.9 μm]	1.4 – 1.6	None

ZrSi#2	ZrSi ₂ [3.9 μm]	2.9 – 3.3	None
ZrSi#3	Zr ₂ Si - ZrSi ₂ [6 μm]	Fully reacted	0.5 – 0.7
ZrSi#4	Zr ₂ Si - ZrSi ₂ [6 μm]	Fully reacted	0.3 – 0.8

3.3.3. Steam Corrosion of ZrSiO₄ Coating

Surface morphology of zircon formed ZrSi₂ coating (ZrSi#5) after the steam corrosion test is presented in Figure 3.24. The low magnification image (Figure 3.24c) show cracks and partial delamination of the surface scale. However, very importantly the EDS result shows that chemical composition of the surface was not altered by the steam corrosion tests. This indicates that the Si in zircon is greatly immobilized during the corrosion process. The high magnification images display that the grain boundaries of zircon phases (Figure 3.24b) was mainly attacked by water vapor so that the surface etching was localized around the grain boundaries (Figure 3.24b). The preferential attack is consistent with the SEM image of corroded bulk ZrSi₂ discussed in section 4.1.2. The corrosion process led to steam infiltration through the boundaries and corrosion of SiO₂ underneath, leading to delamination of zircon grains, however the zircon grains themselves remained resistant to corrosion. It is known that grain boundaries are prone to be attacked due to less stable atomic bonding or accumulation and segregation of impurities [75]. To mitigate the degradation of the zircon layer under steam corrosion, formation of denser and continuous zircon layer is desirable. In future study, optimization of the zircon formation on SiC will be performed by adjusting heat treatment parameters (heating profile and oxygen partial pressure) and composition of zirconium-silicide coatings. For example, Gao et al. reported that better quality and thicker of zircon layer by oxidation of ZrB₂ and SiC composite at 1400 °C under a low oxygen partial pressure (PO₂ = 200 Pa) than ambient air condition [76].

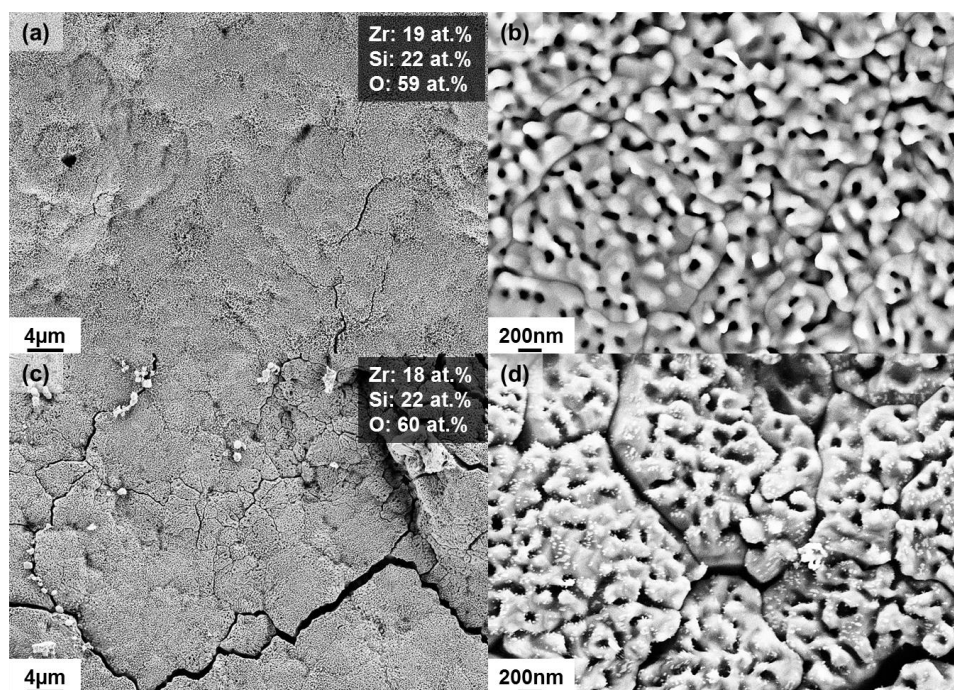


Figure 3.24 Plan-view SEM images of (a-b) as-prepared zircon surface (ZrSi#5) on SiC with magnification, and (c-d) the zircon surface (ZrSi#5) after the steam corrosion test.

Chapter 4: Development Spray Zr-Si Coatings

In addition to the magnetron sputter deposition technique, spraying coating technologies (cold spray and thermal spray) were investigated to make the coating thicker and to increase deposition efficiency. The spray depositions propel powders of coating material at high velocity to target substrate to form a coating. In general, the spray deposition processes are performed in ambient environments and high deposition rates and efficiencies making them conducive to industrial scale-up for various applications. In this section, preliminary results of ZrSi_2 coating on Zirc-4 substrate using cold spray and thermal spray techniques were demonstrated, and the feasibility of these technologies is discussed.

4.1. Cold Spray Coatings

In the cold spray process, solid powder particles of the coating material are accelerated at supersonic velocity (i.e., 2 to 3 Mach) on to the surface of the substrate using pressurized inert gas and a nozzle system. The solid particles experience severe plastic deformation during impact and deposit on the surface. Flat Zirc-4 substrate samples were polished with 320 grit SiC abrasive paper and cleaned prior to the cold spray of ZrSi_2 powder. Pressurized nitrogen at 3.5 MPa was utilized as a carrier gas. Parameters of cold spray process were investigated to optimize coating quality, which were gas pre-heat temperature (e.g., 600 °C, 700 °C, and 800 °C), powder size, and the number of spray passes.

The commercial ZrSi_2 powders produced by oxide reduction and mechanical milling were procured from SCI Engineering Materials. As shown in Figure 4.1a, the as-received powders have irregular shape and a wide size distribution with average size at 20 μm in diameter. EDS analysis and XRD pattern of the powders showed that the major composition of the powder was ZrSi_2 while Si existed as an impurity. Figure 4.1b shows ZrSi_2 particles on Zirc-4 after a preliminary cold spray run. As a ceramic, the powder has a higher hardness (850 HV) compared to Zirc-4 substrate (190 HV). Therefore, deformation and compaction effect were not observed due to a lack of significant plastic deformation of the particles.

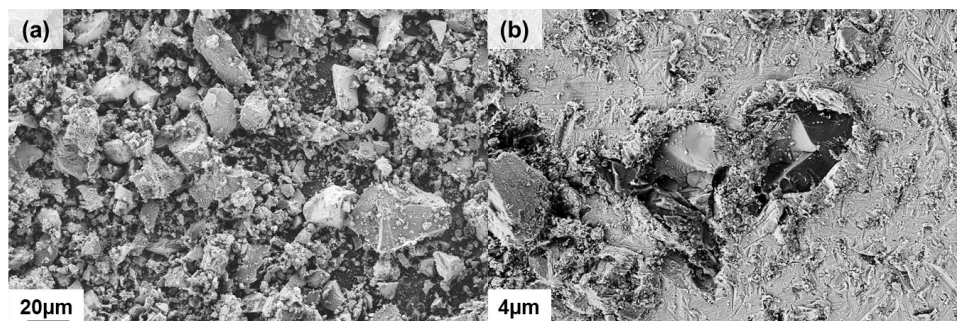


Figure 4.1. SEM plan-view images of (a) as-received ZrSi_2 powder and (b) a local area of ZrSi_2 cold-sprayed coating on Zirc-4 surface.

Figure 4.2 shows the X-ray diffraction patterns for the as-received powder and the cold sprayed coating. The diffraction peaks for the powder and the coating were identical except for the zirconium peaks from the Zirc-4 substrate in the coating. Since the cold spray process was performed in ambient air, any oxidation and phase transformation of the feedstock powder during the deposition process did not occur.

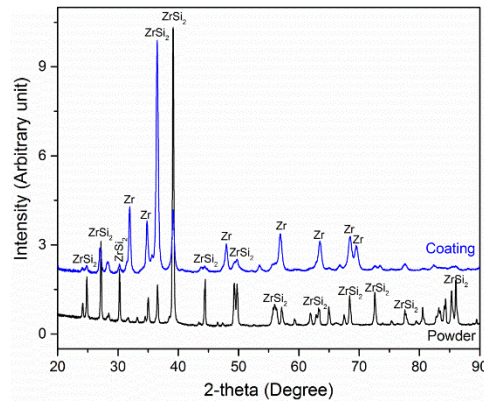


Figure 4.2. X-ray diffraction patterns for as-received ZrSi_2 powders and (b) ZrSi_2 coating deposited by cold spray process.

4.1.1. Effect of Gas Preheat Temperature

The ZrSi_2 powders were sprayed using N_2 gas at 3.5 MPa with gas pre-heat temperatures of 600 °C, 700 °C, and 800 °C. Generally, higher gas pre-heat temperature provides increase in carrier gas velocity, resulting in dense coating. However, the cross-sectional images for the three coating parameters (Figure 4.3) revealed similar thickness of coatings in the range of 5 to 10 μm . The significant roughness in the interface between the substrate and the coating suggests that erosion of the substrate occurred during the spraying process. The lowest gas pre-heat of 600°C had the least erosion, but overall none of the conditions produced a good quality coating.

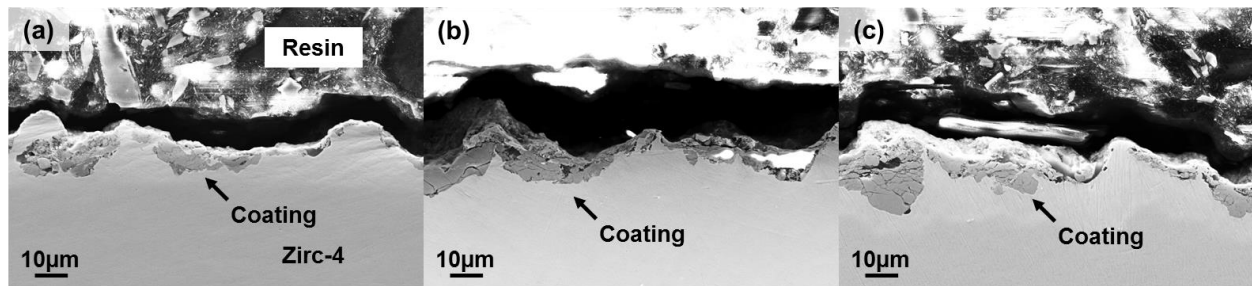


Figure 4.3. Cross-sectional SEM images of cold spray coatings of ZrSi_2 deposited at (a) 600 °C, (b) 700 °C, and (c) 800 °C gas preheat temperatures. Single-pass deposition was used in the spraying process.

4.1.2. Effect of Powder Size

To minimize the substrate erosion, the as-received ZrSi_2 powder was ball-milled using a silicon-nitride vial ball miller for 1 hour and sieved to narrow down the particle size below 25 μm in diameter. As compared to the as-received powder, size of the ball milled powder was distinctively decreased. The effect of the powder size on surface morphology of the coatings and deposition efficiency are shown in the plan-view and cross-sectional SEM images as shown in Figure 4.4 and Figure 4.5. Surface roughness was decreased by spraying the smaller particles so that less substrate erosion was expected. However, the cold spray coatings of the ball-milled powders with various the carrier gas velocities showed substrate erosion and only a thin coating on local areas. while smaller particle sizes led to less roughness, high enough deposition efficiencies were not achieved by using the smaller powders.

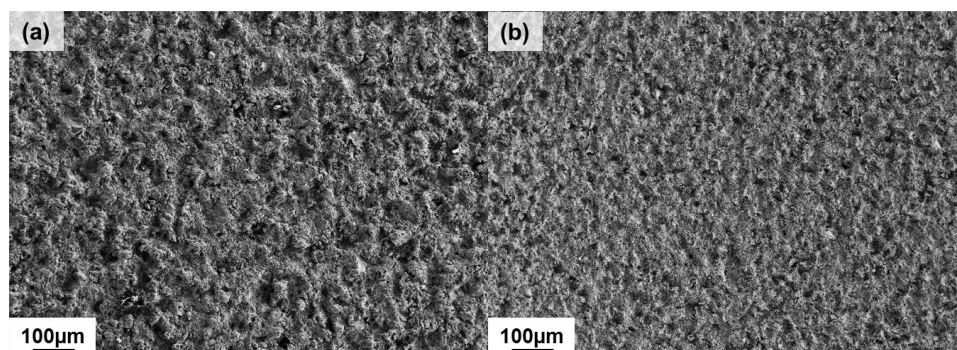


Figure 4.4. SEM plan-view images of (a) ZrSi_2 cold sprayed surface using the as-received powder and (b) the sprayed surface using the ball-milled powder. Two-pass deposition was performed in the both cases.

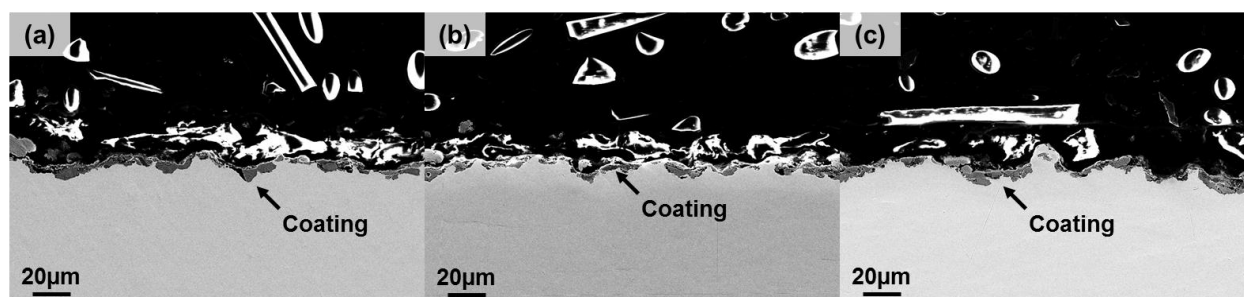


Figure 4.5. SEM cross-sectional images of ZrSi_2 cold sprayed coating with the ball-milled powder at (a) 600 °C, (b) 700 °C, and (c) 800 °C gas pre-heat temperatures. Single-pass deposition was used in the spraying process.

4.1.3. Effect of the Number of Spray Passes

It was postulated that a high flow rate of the ZrSi_2 particles was beneficial to efficiency of the cold spray deposition. Multiple spraying passes (up to four passes) on the substrate were performed at 700 °C gas preheat to increase coating coverage and thickness. However, substrate erosion was still dominant as shown in Figure 4.6. Again, the mechanical properties of ZrSi_2 limit deposition of the powders on Zirc-4 substrate via cold spray technology, at least with the parameters investigated in this study. Therefore, thermal spray deposition which involves melting of the powder particles before spraying was investigated a method to achieve higher deposition rates and with less substrate erosion. The next section summarizes results of preliminary investigation of thermal spray coating of ZrSi_2 on Zirc-4 substrate.

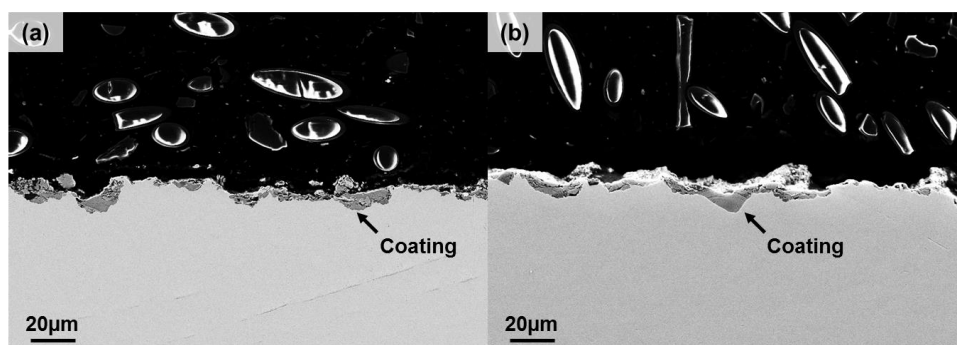


Figure 4.6. SEM cross-sectional images of ZrSi_2 cold spray coating on Zirc-4 substrate at (a) a single pass (b) four passes. The preheat gas temperature was 700 °C.

4.2. Thermal Spray Coatings

In thermal spray process, the feed powders are melted using concentrated heat sources such as plasma and high temperature gas and then the molten particles are propelled on to the substrate surface. After the molten particles impact the substrate, they were cooled rapidly via heat transfer to the substrate to form a coating. The ZrSi_2 powders ($< 44 \mu\text{m}$ in diameter) were heated up by Ar/He mixed gas plasma at atmospheric condition. The thermal spray deposition was performed for 10 passes for each sample to obtain tens of micron thickness. The particles were sprayed by changing a distance between the spraying nozzle and the substrate. Also, the effect of surface finish of Zirc-4 substrate (i.e., grit blast) before the spraying was investigated. Figure 4.7 shows a micron-sized ZrSi_2 splat, a flat disk-shaped morphology, on the coating after the thermal spraying. Even if the original powders had irregular shapes, the high temperature plasma melted and atomized the powders so that they have the spherical shapes before the impact.

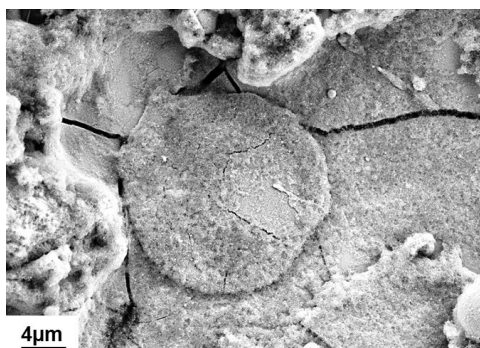


Figure 4.7. SEM plan-view image of a ZrSi_2 splat on thermal sprayed Zirc-4 substrate.

4.2.1. Effect of Spraying Distance

Surface morphology of as-sprayed ZrSi_2 coatings at different spraying distances are shown in Figure 4.8. The coatings were successively formed on the Zirc-4 surface and the top surfaces were significantly rougher than the bare surface. Microcracks and pores can also be seen in these images. However, delamination or spallation of the coatings were not observed. The coating surface with the largest spray distance (i.e., 12.7 cm) appears smoother and flatter than that of the shortest distance (i.e., 7.6 cm). Moreover, the spherical particles were frequently observed on the surface with the shortest distance. The short interaction time of the ZrSi_2 particles and the high temperature plasma (the time for spray powders stay in the plasma flume) could not fully melt the particle. Therefore, some particles may have rebounded or just remained on the top surface in the form of the spherical shapes instead of deposition, leading to a decrease in deposition efficiency.

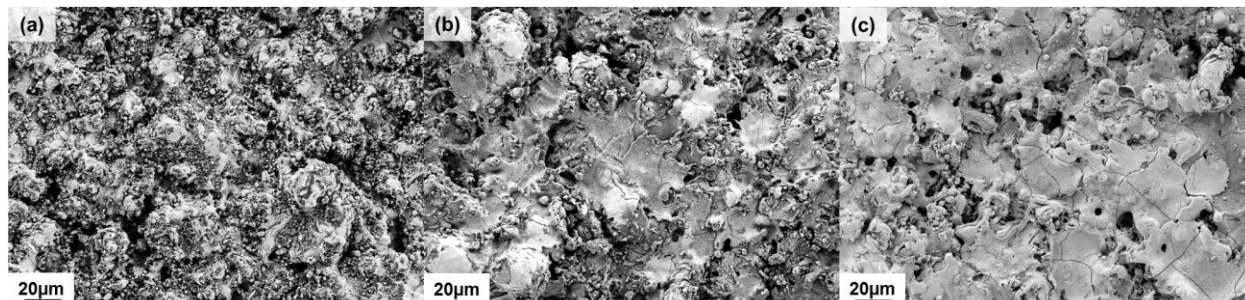


Figure 4.8. Surface morphologies of the ZrSi_2 coatings at different spray distance. (a) 7.6 cm, (b) 10.2 cm, and (c) 12.7 cm.

The cross-sectional SEM images display the microstructures of the thermal sprayed coatings as shown in Figure 4.9. The coating deposited at longer spraying distance were thicker. The 12.7 cm distance parameters produced coating in the range of 50 to 63 μm in thickness but the 7.6 cm spray distance resulted in coating thickness of 40 to 47 μm . It is believed that the powder melting ratio increases with increasing the spray distance to some extent, leading to spreading out of the molten particles when they impact on the surface. Coating defects such as microcracks and pores were identified, which would be detrimental to the oxidation resistance of the coatings. Moreover, the cross-sectional images reveal the contrast difference in the coatings, indicating that the melting and solidification let to thermodynamically dictated segregation of phases in the coatings. It appears that the darker phase represents Si-rich zirconium-silicide and the light phase is made up of Zr-rich zirconium-silicide as would be predicted by the Zr-Si phase diagram.

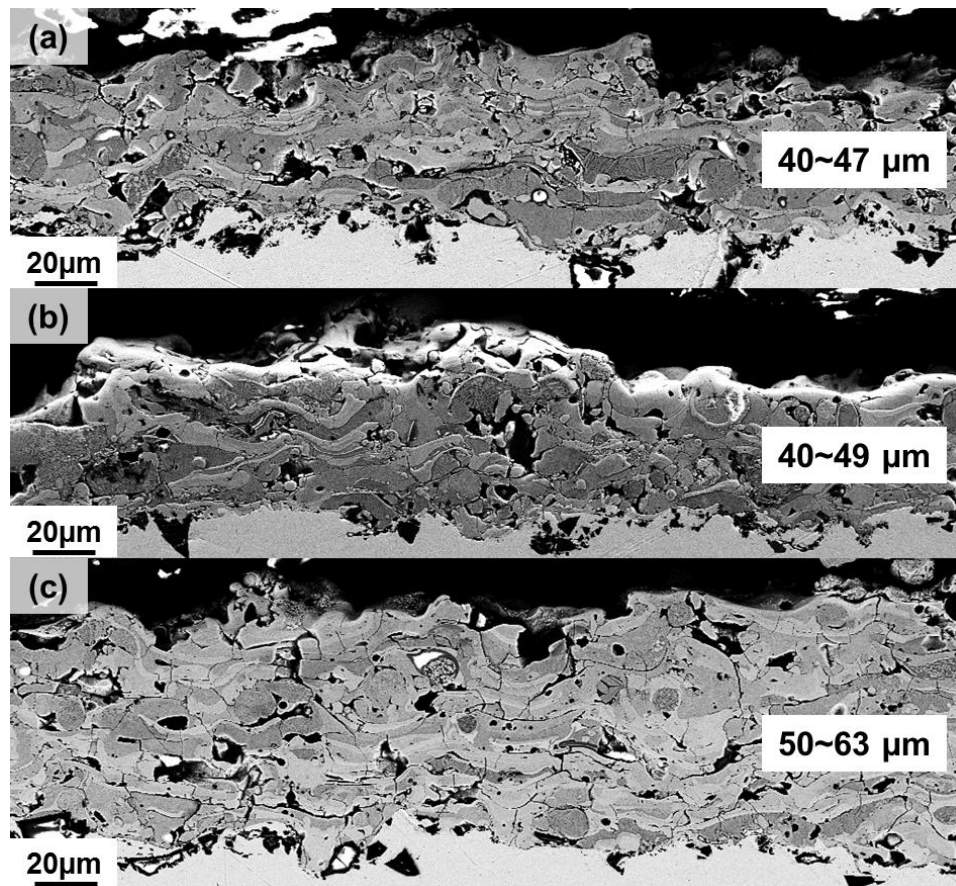


Figure 4.9. SEM image of cross-section of the ZrSi_2 coatings at different spraying distance. (a) 7.6 cm, (b) 10.2 cm, and (c) 12.7 cm.

Figure 4.10 shows surface X-ray diffraction patterns of the thermal sprayed coatings for different spray distances and confirms the phase separation in ZrSi_2 powders during the spraying process. The major phases in the coatings were intermetallic compounds of zirconium-silicides (ZrSi_2 , ZrSi , Zr_5Si_3) and ZrO_2 . The feedstock ZrSi_2 powder undergoes phase changes during the spraying. There was no significant effect of spraying distance on the phases of the thermal sprayed coatings. High magnification of SEM image for the thermal sprayed coating (Figure 4.11a) displays complex microstructures consisting of ZrSi_2 , ZrSi , and Si based on results of EDS analysis, which are in good agreement with the XRD peaks. To investigate formation of the multiple phases in the thermal sprayed coating, bulk ZrSi_2 was melted using Ar arc melter and cooled quickly in ambient air. The cross-sectional image (Figure 4.11b) of the solidified bulk ZrSi_2

displays the complex phases as well, which supports the observations made for the thermal sprayed zirconium-silicide coatings. Therefore, it was concluded that even the high cooling rate of the deposited molten ZrSi_2 particles is not sufficient to prevent phase decomposition. As shown in the Zr-Si phase diagram (Figure 4.11c), ZrSi phase first precipitates from the melt and then ZrSi_2 and Si solidified due to the different melting points (e.g., 1626 °C for ZrSi_2 and 2203 °C for ZrSi).

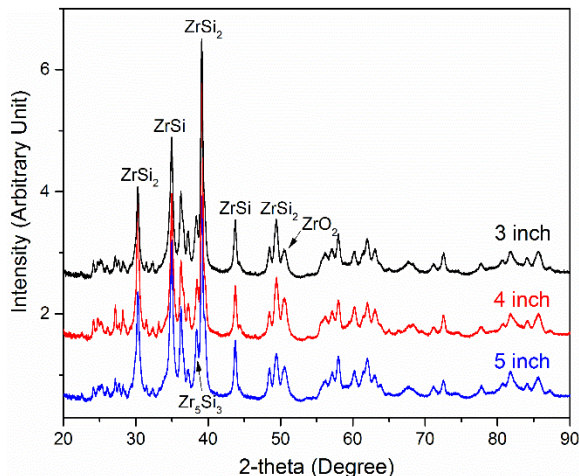


Figure 4.10. XRD patterns of the ZrSi_2 thermal spray coatings prepared using various spraying distances.

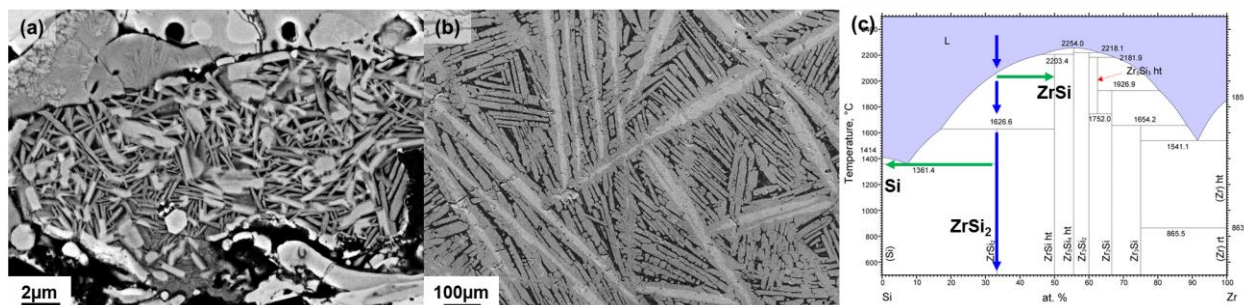


Figure 4.11. SEM cross-sectional image of (a) local area of the thermal sprayed ZrSi_2 coating, (b) arc-melted bulk ZrSi_2 , and (c) Zr-Si binary phase diagram [67] indicating cooling path and possible phase formation.

4.2.2. Effect of Substrate Surface Grit Blasting on Thermal Spray Coating

Effects of the grit blast process were demonstrated by performing thermal spray for Zirc-4 surface without grit blast process. While the previous thermal spray runs were performed after grit blasting, thermal spray coatings were also investigated after finishing the surface with only 320 grit SiC abrasive paper. The cross-sectional image of the coating (Figure 4.12) displayed spallation of coating due to the weaker adhesion between the coating and the substrate. Mechanical interlocking of the coating appeared to be improved by the roughened surface, resulting in strong adhesion.

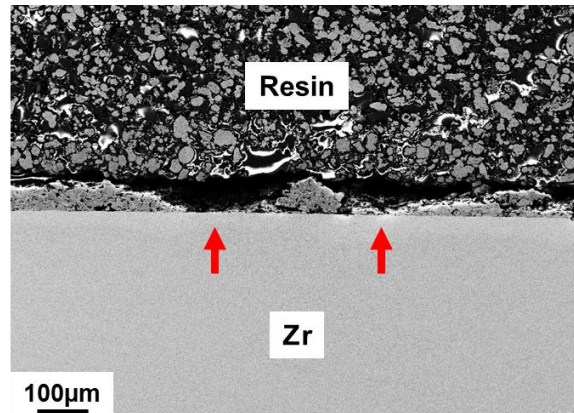


Figure 4.12. Cross-sectional image of thermal spray coating of ZrSi_2 without grit blast of Zirc-4 substrate. The red arrows indicate the local area showing coating damages during sample preparations. Only 320 grit SiC grinding was used.

The thermal sprayed ZrSi_2 coating (deposited at 7.6 cm distance and 10 passes) was exposed at 700 °C air for 10 hours to evaluate its oxidation behavior. After the oxidation, the coating was delaminated and surface oxidation of Zirc-4 substrate was observed as shown in Figure 4.13. It is speculated that oxygen infiltrated through the cracks and pores in the as-deposited coating and reacted with the substrate. The substrate oxidation resulted in the delamination of the coating. Thermal spray technique is efficient method to deposit ZrSi_2 but further optimization process is required to make the coatings thicker and more homogeneous and dense to realize the full benefits of the coating.



Figure 4.13. Photograph of oxidized thermal spraying (ZrSi_2 coating) at 700 °C air for 10 hours. Coating delamination was clearly identified.

Chapter 5: Development of Slurry Zr-Si Coatings

5.1. Investigation of Processing Condition for Zr-Si Coatings

5.1.1. Initial Investigation

Ceramic Matrix Composite (CMC) coatings via Polymer Derived Ceramic (PDC) slurry techniques have been characterized for their bulk components to confirm the theoretical siloxane polymer-filler ratios in extreme conditions (1000 °C) for bulk samples. Due to the lower ceramic yield of poly(dimethylsiloxane) (PDMS) ceramic products, it was determined that poly(methylhydrosiloxane) (PMHS) was the better silicon base material for further investigative studies. Initial CMC coatings were performed on pure silicon substrates. Silicon wafers were polished using 400 grit SiC polishing paper and cleaned prior to coating application. Silicon was chosen as an initial investigation substrate material because it has similarly low thermal expansion properties to Zircaloy-4 and was expected to have strong adherence properties due to the silicate base material in the precursor suspension fluid.

Initial CMC characterizations for the ZrSi_2 -PMHS component were performed using the theoretical filler-polymer volume percentages of 31% ZrSi_2 filler component. After applying the coatings, samples were cured and pyrolyzed at either 800 °C or 1000 °C for 2 hours. Figure 5.1 details the surface imaging of each of these samples after their respective pyrolysis. It is clear from the SEM plain-view imaging that there is a significant degradation of the matrix when pyrolyzed at 1000 °C as compared to 800 °C pyrolyzed samples which had an intact SiOC matrix at the surface of the CMC coating. At 800 °C, the intact matrix acts as an encapsulating material for a cohesive matrix. At each temperature, the adhesion of the ceramic coating is strong with only minor spallation occurring on the 1000 °C pyrolyzed sample due to a “lipping” effect created during hand dipping.

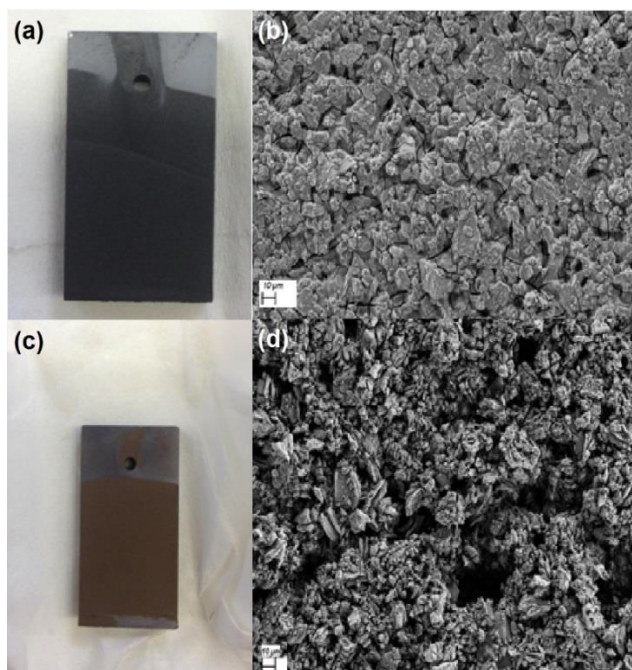


Figure 5.1. Initial Coating Tests for (a,b) 800 °C and (c,d) 1000 °C Pyrolysis on Pure Silicon Substrates.

Figure 5.2 shows the TYPE-0 31% ZrSi_2 -PMHS sample after 800 °C pyrolysis. It can be observed that a clear and apparent “matrix” is established in the coating consisting of a silicon, oxygen, and carbon and ZrSi_2 filler particles dispersed throughout the matrix. The filler particles did not show evidence for matrix

inhomogeneity such as particle agglomerations or particle sedimentation within the coating during the coating and curing stages prior to matrix stabilization and phase transformation. However, it is evident that the large particle size distribution (PSD) observed in TYPE-0 ZrSi_2 fillers limits the homogeneity and the amount of dense packing throughout the CMC. The initial slurry coating tests for TYPE-0 31% ZrSi_2 -PMHS revealed an elemental break down for the material components for the CMC coating. The 800 °C pyrolysis process resulted in a high density SiOC matrix which acts as a binding material for the ZrSi_2 filler particles. The SiOC matrix was determined to have an atomic composition of $\text{SiO}_{1.19}\text{C}_{0.13}$ after 800 °C pyrolysis using EDS.

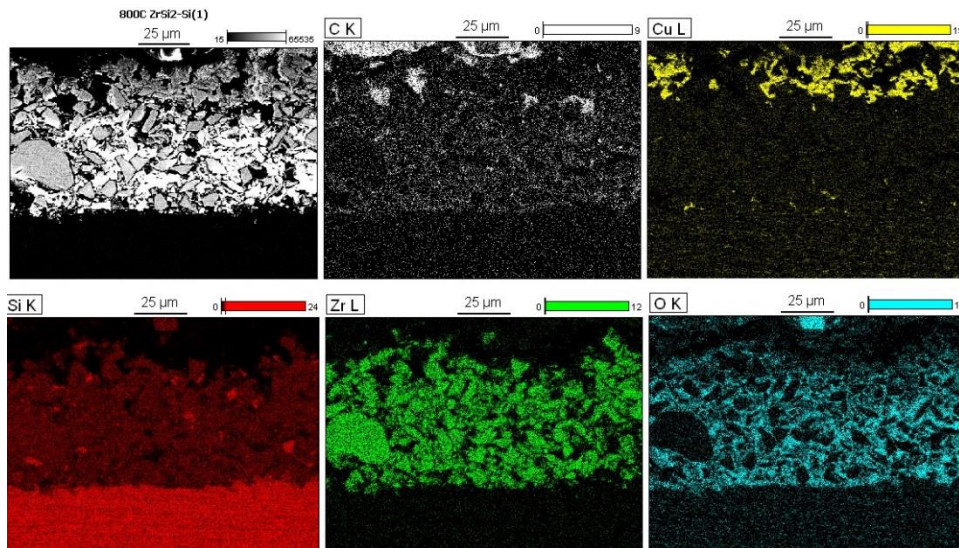


Figure 5.2. EDS Elemental Mapping for Cross-Section Image of 31% Filler Volume (TYPE-0) ZrSi_2 -PMHS Composite on Silicon Substrate.

5.1.2. Effect of Temperature on Evolution of Slurry Coatings

The processing conditions for slurry coatings, as mentioned previously, strongly influences the materials ability to adhere to a given substrate material, have advantageous mechanical and structural properties, and limit negative side effects to the substrate (e.g. thick oxide growth on the surface of Zircaloy-4). Thus, an investigation on the impact of a range of pyrolysis temperatures including 200, 400, 500, 600, 800, and 1000 °C were tested to observe the impact which pyrolysis temperature has on the chemical, phase, and structural aspects of the composite coating as well as the effects on which these possible processing conditions have on the underlying Zircaloy-4 substrate.

Understanding the temperature evolution of the ZrSi_2 -PMHS at various pyrolysis processing temperatures was critical for determining the ideal processing environment. Figure 5.3a displays the X-ray diffraction (XRD) spectrums for TYPE-1 31% ZrSi_2 -PMHS (ideal volume ratio) coatings on Zr-alloy after pyrolysis. All pyrolysis temperature tests were performed for 2 hours in dry air. Oxidation of ZrSi_2 filler particles is initially observed by reduction of ZrSi_2 peak intensity between 500C – 600 °C. The ZrO_2 peak intensity rapidly increases between 600 °C-800 °C pyrolysis conditions. The significant increase in ZrO_2 formation at 800 °C pyrolysis is indicative of the rapid increase in ZrSi_2 oxidation rate at 800 °C. However, analysis of 0% ZrSi_2 -PMHS coated on Zr-alloy using XRD, observed in Figure 5.3b, which confirmed that formation of ZrO_2 formation due to oxide growth on the Zr-alloy substrate was significantly increased at 800 °C. The formation of SiO_2 is minimal during 600 °C pyrolysis but peak intensity is greatly increased at 800 °C and 1000 °C pyrolysis. The identification of SiO_2 crystalline structures at these conditions is

reflective of the increase in oxidation of ZrSi_2 filler particles and decomposition of the SiOC matrix. The decomposition of the crosslinked silicon based polymer results in the splicing of the Si-O-C matrix bonds by: $\text{SiO}_x\text{C}_y \xrightarrow{\Delta} \text{SiO}_2 + \text{SiC} + \text{C}$. The decomposition is evident at 800 °C and 1000 °C by the observance of both SiO_2 and SiC peaks with increasing intensity. This is confirmed by XRD analysis of pure PMHS samples. The degradation of PMHS and observable SiC and SiO_2 peaks is negligible below 800 °C.

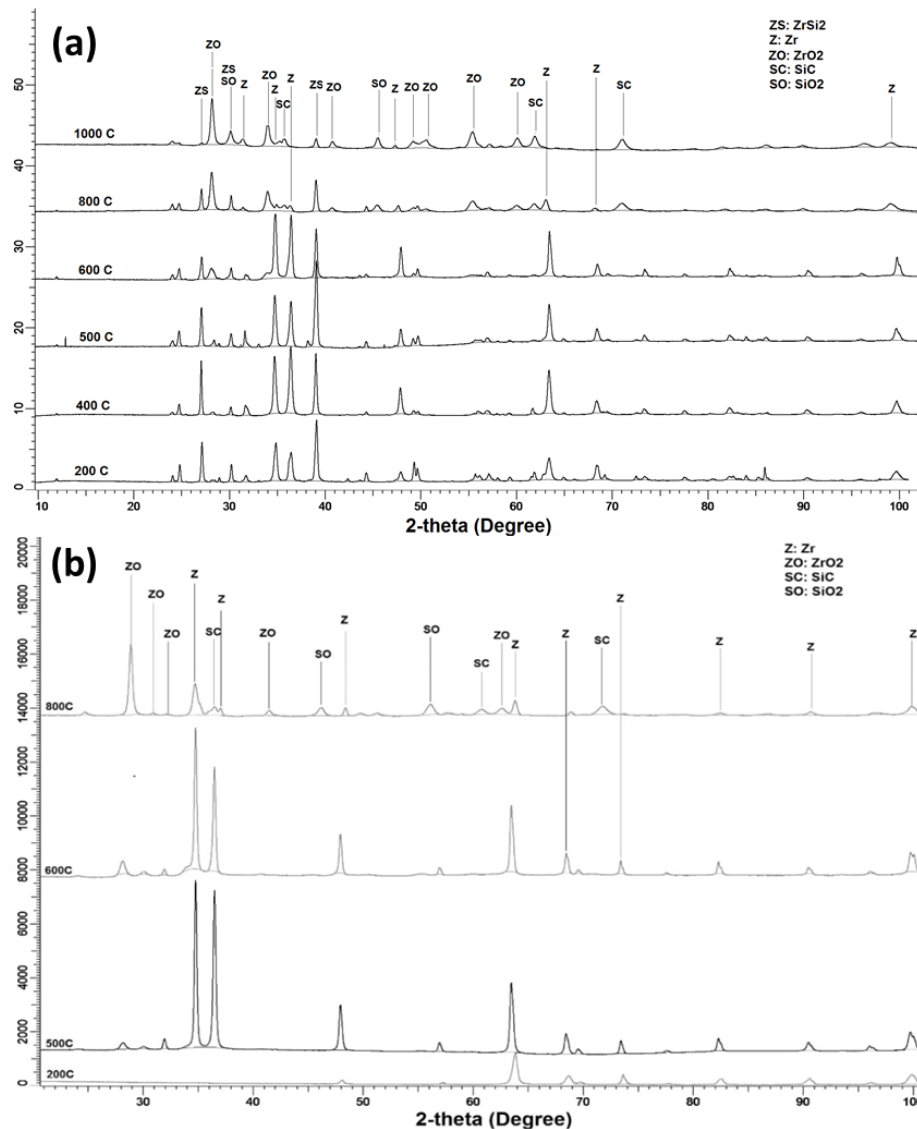


Figure 5.3. (a) X-ray Diffraction (XRD) Full Scan Pyrolysis Temperature Evolution of 31%ZrSi₂-PMHS on Zircaloy-4 in Air and (b) PMHS on Zircaloy-4 in Air (no ZrSi₂ filler).

The temperature evolution of the ZrSi_2 -PMHS CMC coating was also analyzed using FT-IR by analyzing infrared absorbance intensities with respect to wavelength to identify molecular bonding structures within the ceramic coating. FT-IR spectroscopy is often used to analyze polymers (organic and inorganic) for bonding evolution during curing and pyrolysis as the two-dimensional polymers transform into a complex three-dimensional framework. At elevated temperatures, inorganic polymers, such as PMHS, degrade due to bond cleaving producing nanocrystalline products. The systematic evolution and degradation of the

amorphous and crystalline phases of the polymer precursor and filler matrix system can be observed using FT-IR techniques. The results of the FTIR analysis are observable in Figure 5.4.

The FT-IR spectrum of PMHS is dominated by the strong Si-O absorption peaks at wavelengths of $\nu 1020\text{cm}^{-1}$ and $\nu 1240\text{cm}^{-1}$ that originate in the siloxane backbone and shift after curing into the three-dimensional amorphous matrix structure. The initial peaks of $\sim\nu 1050\text{cm}^{-1}$ and $\sim\nu 1110\text{cm}^{-1}$ Si-O absorption bands at 200°C are shifted to $\sim\nu 1100\text{cm}^{-1}$ and $\sim\nu 1230\text{cm}^{-1}$. A distinct shift was observed between 600°C and 800°C corresponding to a large change in bonding structure during pyrolysis at temperatures 800°C and greater. It is evident that this distinct shift is due to the degradation and semi-crystallization of the Si-O-C matrix to SiO_2 and SiC products. This is evident due to the formation of a distinct weak, broad Si-C peak formed at $\sim\nu 800\text{cm}^{-1}$. The degradation of the matrix, release of volatile gases, and formation of residual nanocrystalline structures occurs in stages depending on the temperature in which pyrolysis occurs. It is observed that hydrogen function groups (Si-H) which were not completely removed during curing were completely removed when pyrolyzed at 400°C and above as evident of the removal of the weak, broad peak at $\nu 2170\text{cm}^{-1}$. The complete methyl ($-\text{CH}_3$) functional group removal is not achieved until pyrolysis at 800°C . The Si- CH_3 band at $\nu 1280\text{cm}^{-1}$ is distinct with minimal reduction until 800°C . Also, it is evident that there is absorbed water molecules or hydroxy group bonding ($-\text{OH}$) in the ceramic due to wide bands at $\sim 3400\text{cm}^{-1}$ (not included) and 1640cm^{-1} .

The absorption domain ranging between 450 and 1000cm^{-1} has three observable peaks at $\nu 463\text{cm}^{-1}$, $\nu 670\text{cm}^{-1}$, and $\nu 960\text{cm}^{-1}$ corresponding to the zirconium silicide bonding structure evolution. The strong, broad $\nu 463\text{cm}^{-1}$ absorption peak has a slight observable growth at 600°C and greatly increases in intensity at 800°C and is attributed to the Zr-O-Zr stretching vibration due to the formation of zirconium oxo network. The small, narrow $\nu 670\text{cm}^{-1}$ absorption peak is attributed to Zr- O_2 -Zr band stretching. The $\nu 960\text{cm}^{-1}$ shoulder peak had a significant growth at 800°C which is evidence of an intermediate Si-O-Zr bonding structure.

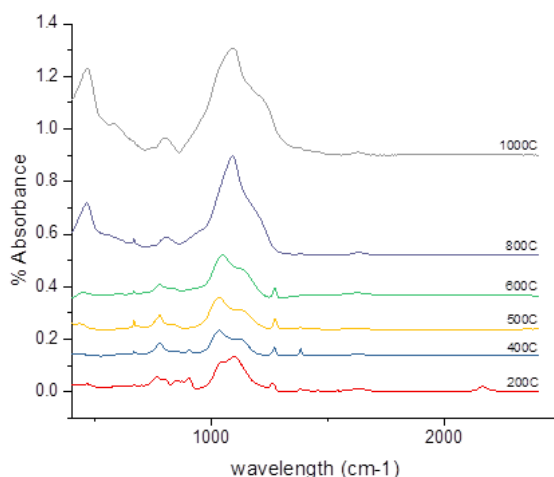


Figure 5.4. ZrSi₂-PMHS Ceramic System FT-IR Band Evolution at Processing Temperatures 200°C – 1000°C .

The plain-view images of the surface topography changes of the TYPE-1 31%ZrSi₂-PMHS coating after pyrolysis (500°C , 600°C , 800°C and 1000°C for 2 hours) are depicted in Figure 5.5. There is a noticeable increase in superficial surface cracks due to processing stresses and degradation at 800°C and 1000°C . These cracks are likely due to the increase in released gases from methyl group removal (i.e. CH_4 , CO , CO_2 , and H_2) and matrix shrinkage. There is also evidence of crack removal between the temperatures of 500°C and 600°C . The elimination of surface cracks at 600°C could be evidence of self-healing behavior of the polymer prior to degradation. Although, this hypothesis would require further investigation to

confirm. This phenomena confirmation would be significant for nuclear environment applications due to low temperature (300 °C), steam environmental conditions. Limiting superficial surface cracks in corrosive or harsh, low temperature environments could lead to a greater reduction of harmful species permeation through the coating.

It is evident that the pyrolysis temperature greatly effects the ceramic coating structure, but it was also evident that adherence of the coating to the Zircaloy-4 substrate was also greatly affected by the pyrolysis temperature. Samples pyrolyzed at 400 °C and 500 °C in air experienced adherence defects and resulted in significant coating loss during handling and measurements. Samples pyrolyzed at 1000 °C underwent significant degradation and rapid macroscale cracks, exposing the oxidized substrate surface underneath. Optimal pyrolysis temperatures were determined to be between 600 °C-800 °C. Macroscale analysis of coating surfaces show a clear “bubbling” in pure PMHS coatings while filler matrix coatings are much smoother. All coatings exhibit strong substrate adhesion. There is evidence of peeling at the bottom of some substrates due to “lipping” effects during dip coating. This is an issue due to hand dipping. This technique is advantageous due to its simplicity but can affect homogeneity of coating thickness and “lipping” due to non-consistent dipping velocity.

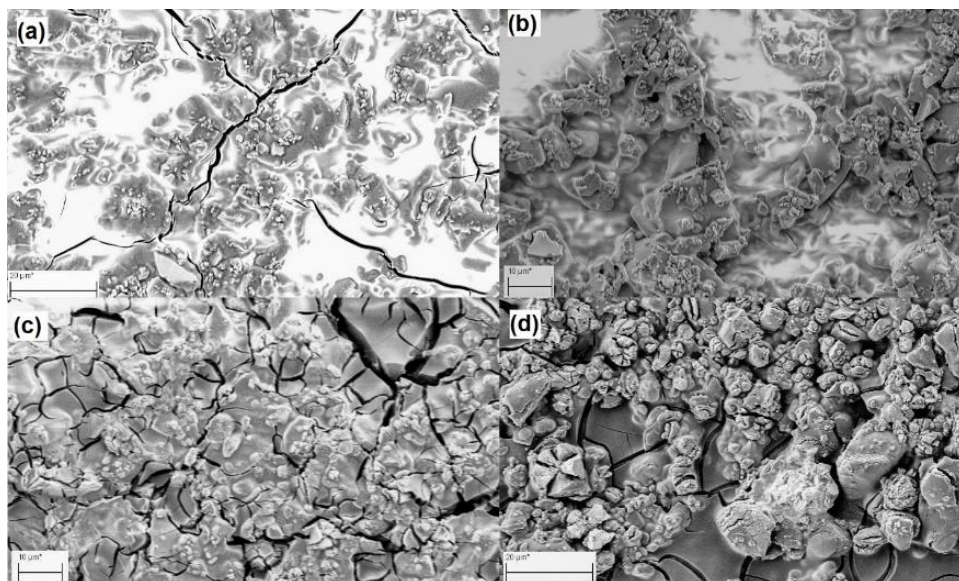


Figure 5.5. SEM Plan-View Images of 31%ZrSi₂ -PMHS Coatings After (a) 500 °C Pyrolysis, (b) 600 °C Pyrolysis, (c) 800 °C Pyrolysis, (d) 1000 °C Pyrolysis.

5.1.3. Processing Environmental Effects

The processing atmosphere was also investigated. The environments investigated to oppose the curing and pyrolysis in an O₂ rich (air) environment was an inert crosslinking and pyrolysis environment and an oxidative curing environment with an inert pyrolysis environment. Below 700 °C, it is assumed that N₂ atmospheres can be considered inert.

The atmosphere differences were investigated using a thermogravimetric analysis (TGA) technique. Oxygen rich curing shows an increase in weight during the dwell time at the curing temperature (150 °C) after initial slurry drying. The resulting weight gain is due to the addition of oxygen molecules to crosslink silicone polymer chains via Si-O-Si bonding to form the amorphous, high density SiOC matrix (prior to ceramic transformation). In comparison, inert environment “curing” resulted in a weight loss of approximately 45% during curing and up to 200 °C. The weight loss below 200 °C can be assumed to be

completely attributed to the removal of organic solvent and PMHS decomposition, the loss of PMHS species is >90%. The significant loss in in weight is due to the nearly complete removal of organic functional group and oxygen within the siloxane polymer due to Si-O intramolecular bonding. The forced intramolecular crosslinking in inert environments results in a higher amount of matrix shrinkage, as opposed to crosslinking via hydrolysis in an oxidative environment which allows the matrix the reduce mass and volume loss. The weight loss above 200 °C was negligible in inert conditions. This shows that the matrix was completely degraded and condensed at ~200 °C.

Pyrolysis atmospheres (inert versus oxidative) was also investigated after curing at 150 °C in an oxygen rich environment. The inert pyrolysis sample had little weight change effect as compared to the oxygen rich environment below 700 °C (i.e. before significant ZrSi₂ particle oxidation). The difference in weight percentage is approximately 5% at 500 °C. This difference is likely due to oxygen bonding during organic species removal at elevated temperatures for the oxygen rich environment sample whereas the inert pyrolysis sample does not have O₂ atmosphere reactions to compensate for organic molecule loss. While crosslinking in an inert environment is not advantageous due to the significant weight loss and resulting coating breakdown at low temperatures, pyrolysis in an inert environment is of interest due to the SiOC matrix structural integrity from oxygen rich atmosphere intermolecular crosslinking (as observed in TGA experiments).

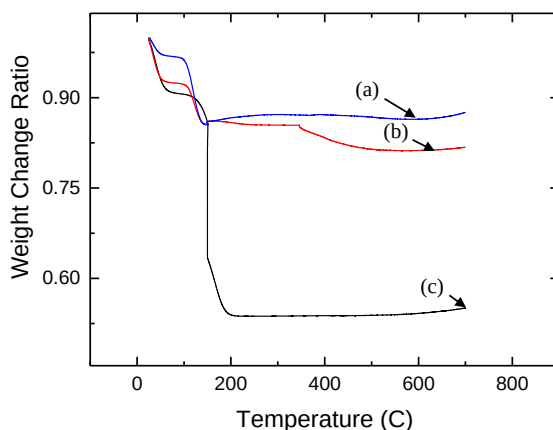


Figure 5.6. Thermogravimetric Analysis (TGA) processing environment analysis for TYPE-1 31%ZrSi₂-PMHS (a) oxygen rich environment curing & pyrolysis, (b) oxygen rich curing & inert environment pyrolysis, (c) inert environment curing & pyrolysis.

The filler volume ratio was also investigated for potential TYPE-1 ZrSi₂-PMHS coatings. The first investigation was into the weight change of the slurry coating based on filler amount using TGA techniques (Figure 5.7).

It is observable that slurry drying occurs in two steps, the first occurring below 75 °C and the second between 100 °C and 150 °C prior to curing. The drying refers to the removal of n-Octane organic solvent. The results show that the organic solvent is not completely removed prior to curing since the solvent was added at 20 wt.% for each slurry. During curing, there is a slight weight gain for each sample due to oxygen facilitated crosslinking. During degassing (150-600 °C) there is very little weight changes due to the rate of oxygen addition in the SiOC matrix and the removal of volatile organic functional groups by off gassing. Lastly, ZrSi₂ filler particle oxidation occurs at an increasing rate between 600 °C and 800 °C.

The filler oxidation rates are the same for all filler volume ratios but, due to difference in filler amounts, the mass change and net filler volume increase is greatly increase with filler volume ratio. This has a potential to cause thermal stresses within the coating between SiOC matrix and filler expansion or result in

a residue porosity. Therefore, at temperatures above 600 °C, the amount of filler particles in the slurry can significantly affect the expansion-shrinkage characteristics of the ceramic as well as the integrity of the matrix.

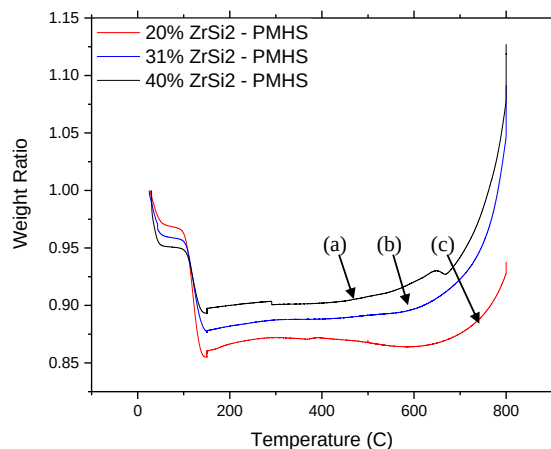


Figure 5.7. Thermogravimetric Analysis (TGA) Slurry Comparison for Filler Volume Percentage and the Effects on Composite Components for (a) 40%ZrSi₂-PMHS, (b) 31%ZrSi₂-PMHS, (c) 20%ZrSi₂-PMHS.

Figure 5.8 shows the difference in coating filler volume between TYPE-1 20, 31, and 40% ZrSi₂ filler volume and pure PMHS after pyrolysis at 600 °C and 800 °C. Macroscale analysis of coating surfaces show a clear “bubbling” in pure PMHS coatings while filler matrix coatings are much smoother. All coatings exhibit strong adhesive properties to the Zircaloy-4 substrates. There is evidence of peeling on the bottom of some substrates due to “lipping” effect during dip coating. This is simply an issue as a result to hand dipping. This technique is advantageous due to its simplicity but can affect homogeneity of coating thickness and cause “lipping” to occur due to a non-constant dipping velocity.

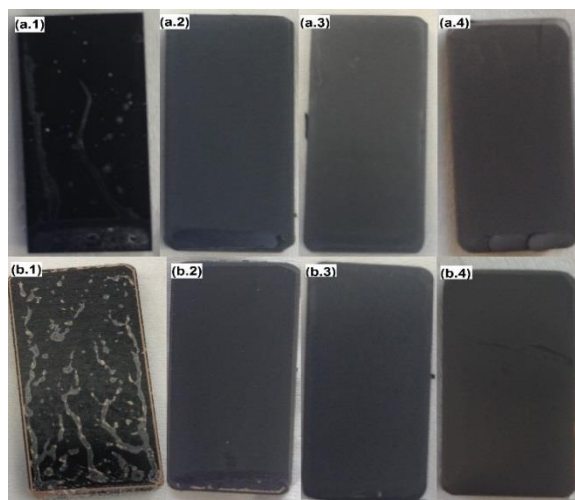


Figure 5.8. Substrate Images of (a) 600 °C Pyrolysis and (b) 800 °C Pyrolysis for (1) PMHS, (2) 20%ZrSi₂-PMHS, (3) 31%ZrSi₂-PMHS & (4) 40%ZrSi₂-PMHS.

Oxidation of the underlying Zircaloy-4 substrate when exposed to slurry processing temperatures is potentially problematic since the intent of this investigation is to limit the oxidation growth on the substrate at temperatures greater than 800 °C. The oxide can form much more easily during processing as compared to the oxide growth after processing. This is due to the transient porosity during processing which allows

volatile organic gases to escape from within the matrix but can easily allow oxygen from the atmosphere to permeate through the ceramic matrix coating. Therefore, it is of interest to analyze the oxide growth during processing as well as the ceramic matrix coating characteristics. Figure 5.9 depicts a comparison of TYPE-1 20, 31, and 40% ZrSi₂-PMHS and TYPE-0 31%ZrSi₂-PMHS coated samples on Zircaloy-4 after 800 °C pyrolysis for 2 hours. The use of TYPE-0 (> 1 μm) particles resulted in poor homogeneity, higher surface roughness and larger oxide growth during processing than TYPE-1 ceramic matrix coatings.

The TYPE-1 samples showed a correlation between the increase filler volume percentage and the increase in observable residual porosity within the ceramic matrix coating. For example, the 40% filler volume sample exhibited cross-sectional area porosity of approximately 7% pore area while the 20% filler volume sample had a porosity less than 3%. Also, the porosity of the TYPE-1 40% filler volume sample and the TYPE-0 sample had large pore formation while the TYPE-1 20% filler volume sample had “pores” in the form of micro cracks.

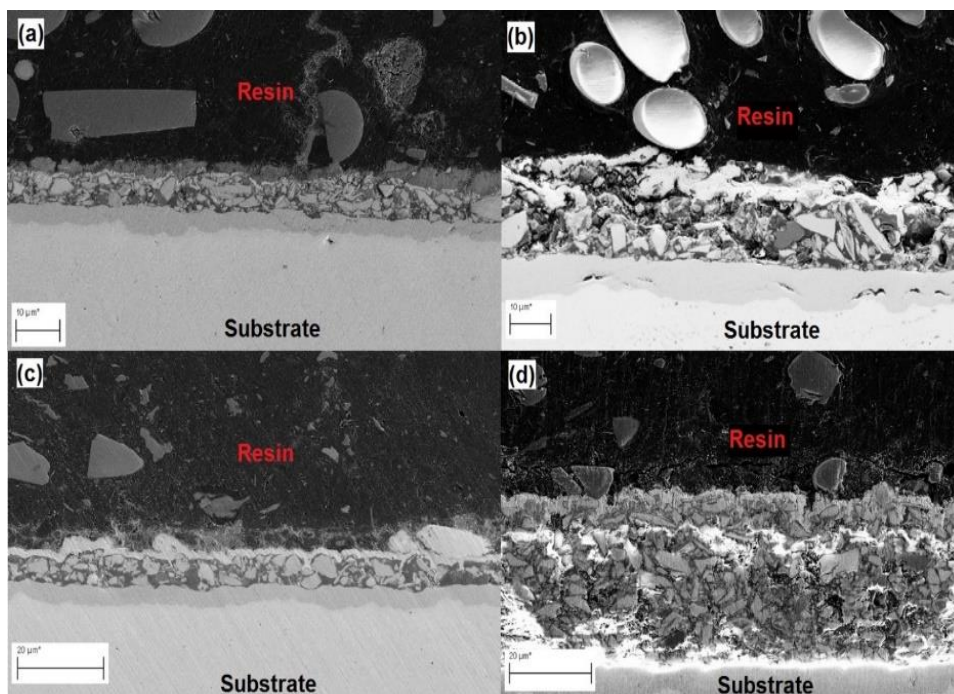


Figure 5.9. SEM Cross-Sectional Images of 800 °C in Air Pyrolysis for (a) 31%ZrSi₂-PMHS, (b) Large Particle 31%ZrSi₂-PMHS, (c) 20%ZrSi₂-PMHS, (d) 40%ZrSi₂-PMHS on Zircaloy-4.

The oxygen growth comparisons can be observed in Figure 5.10 and Table 5.1 for filler volume ratios and filler particle size for processing of TYPE-1 and TYPE-0 ZrSi₂-PMHS coatings with respect to pure PMHS coated and bare Zircaloy-4 samples in the same environment. At 500 °C and 600 °C there is very little observable oxidation growth difference between the analyzed coated substrates and bare Zircaloy-4. This is an indication of the transient porosity at these temperatures, allowing oxygen to permeate through the coating to easily oxidize the underlying substrate. A significant change in protection can be observed at 800 °C pyrolysis conditions. There is a significant amount of oxidation reduction at 800 °C with the lowest amount of protecting being from pure PMHS which results in a 53% oxide growth reduction. TYPE-1 particle coatings at 800 °C pyrolysis reduces oxide growth by ~33% better than TYPE-0 particle composites of similar filler volume ratio. An increase in pore percentage allows for more oxygen permeation through the composite coating.

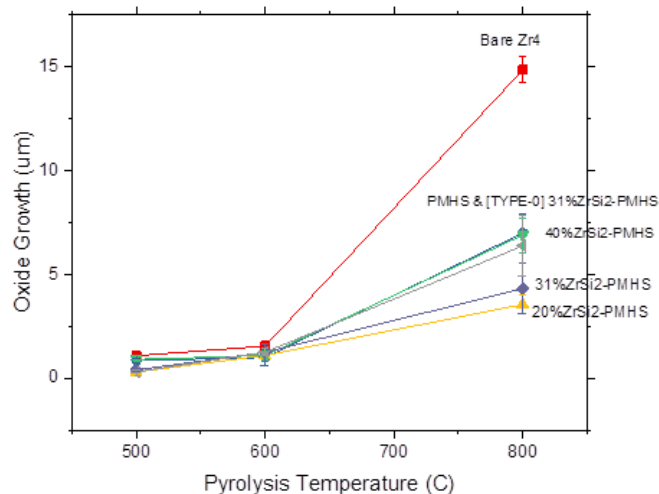


Figure 5.10. Pyrolyzed ZrSi₂-PMHS Systems on Zircalloy-4 Oxide Growth Thickness Comparison.

Table 5.1. Pyrolysis Processing Temperature Substrate Oxide Growth Comparison for ZrSi₂-PMHS Composites on Zircalloy-4 Substrates.

Surface Coating	500 °C	600 °C	800 °C	1000 °C
[TYPE-0] ZrSi ₂ -PMHS (30 vol.%)	0.9 μm	1.09 +/- 0.201 μm	6.90 +/- 0.834 μm	150-180 μm
[TYPE-1] ZrSi ₂ -PMHS (20 vol.%)	0.40 +/- 0.084 μm	1.24 +/- 0.415 μm	4.31 +/- 1.206 μm	-
[TYPE-1] ZrSi ₂ -PMHS (31 vol.%)	0.29 +/- 0.083 μm	1.09 +/- 0.188 μm	3.55 +/- 0.475 μm	-
[TYPE-1] ZrSi ₂ -PMHS (40 vol.%)	0.30 +/- 0.059 μm	1.25 +/- 0.175 μm	6.37 +/- 1.456 μm	-
PMHS	0.84 +/- 0.111 μm	1.00 +/- 0.400 μm	6.99 +/- 0.936 μm	-
BARE	1.08 +/- 0.140 μm	1.54 +/- 0.261 μm	14.85 +/- 0.625 μm	-

The optimal pyrolysis temperature for the polymer derived coatings on Zircalloy-4 was determined to be 600 °C. The matrix integrity observed at 600 °C was found to be optimal due to the minimization of surface flaws (i.e. cracks). Also, 600 °C pyrolysis allowed for transient pore reduction to occur via oxidation of ZrSi₂ particles and matrix shrinkage without significant oxidation to occur while transient pores were formed.

5.2. Oxidation and Steam Corrosion of Slurry Coatings

Oxidation protection tests were performed in high temperature air atmospheres at 800 °C and 1000 °C. The oxidation protection was investigated for substrates coated with TYPE-2 20%, 31%, and 40% ZrSi₂-PMHS slurry mixtures (fine ZrSi₂ powder). TYPE-1 coatings (micron-scale filler parties) are not introduced in this report due to no significant success. The oxide growth tests were analyzed for samples after 2, 5, 10, and 20 hours exposure at 800 °C and 1 hour at 1000 °C in air atmospheres.

5.2.1. Fine Filler Particle Oxidation Protection

TYPE-2 ZrSi₂-PMHS coatings were developed to investigate the effects of using fine grain (FG) filler particles instead of micron scale particles. Figure 5.11 shows the difference in particles size between the micron scale particles and the fine grain (FG) particles. The additional attrition milling time reduced the average particle size from ~ 1.5 μm to ~ 0.7 μm. It also resulted in a significant reduction of maximum

particle size, from 8 - 10 μm to 3 μm . The reduction in particle size distribution is significant in increasing the homogeneity of the resulting ceramic matrix coating (CMC) as well as decreasing surface flaws (cracks, spallation, etc.).

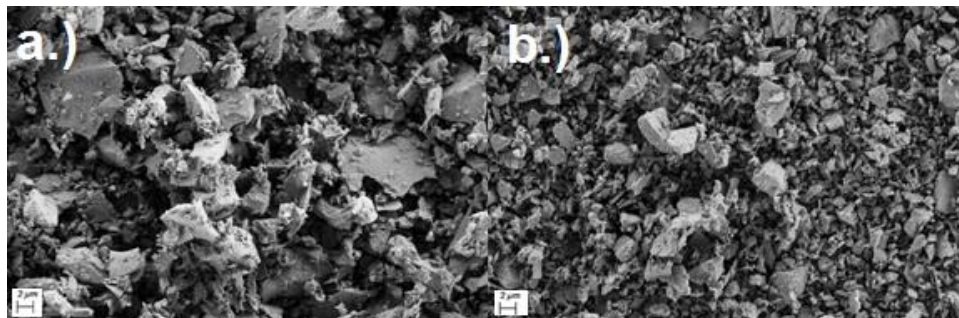


Figure 5.11. SEM Image of the ZrSi_2 Particle Size Distribution Comparison for (a) [TYPE-1] Micron Scale Composite Filler Particles and (b) [TYPE-2] FG Composite Filler Particles.

Figure 5.12 shows an example of TYPE-2 ZrSi_2 -PMHS samples using 20%, 31% and 40% [by volume] FG particles. Samples with FG particles exhibited less spallation due to the “lipping” effect. The TYPE-2 coatings were also found to be slightly thicker than TYPE-1 coatings using similar withdraw speeds.

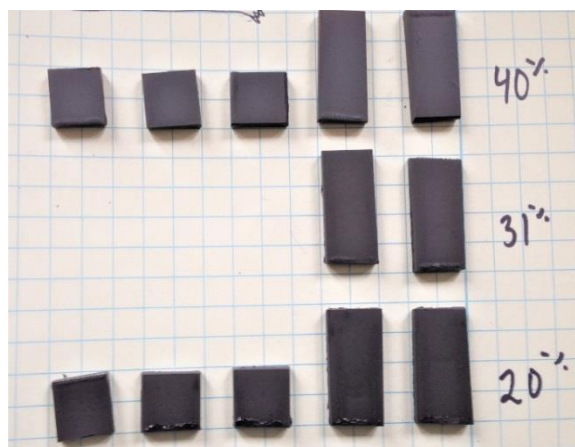


Figure 5.12. Photograph of ZrSi_2 – PMHS [TYPE-2] Filler Composites after 600 °C Pyrolysis.

TYPE-2 substrates resulted in coatings with a reduced porosity, increased homogeneity, and a coating with greater thickness uniformity. The FG filler particle CMCs were therefore much denser than the TYPE-1 coatings and had a greater uniformity of particle distribution throughout the ceramic structure. The TYPE-2 coatings tended to have a thickness of 10-20 μm . Figure 5.13 is an example of a TYPE-2 31% ZrSi_2 – PMHS coating after 600 °C pyrolysis which had a uniform coating thickness of approximately 11 μm . The homogeneity of the particle dispersion also resulted in less surface cracks penetrating a significant distance into the coating after processing.

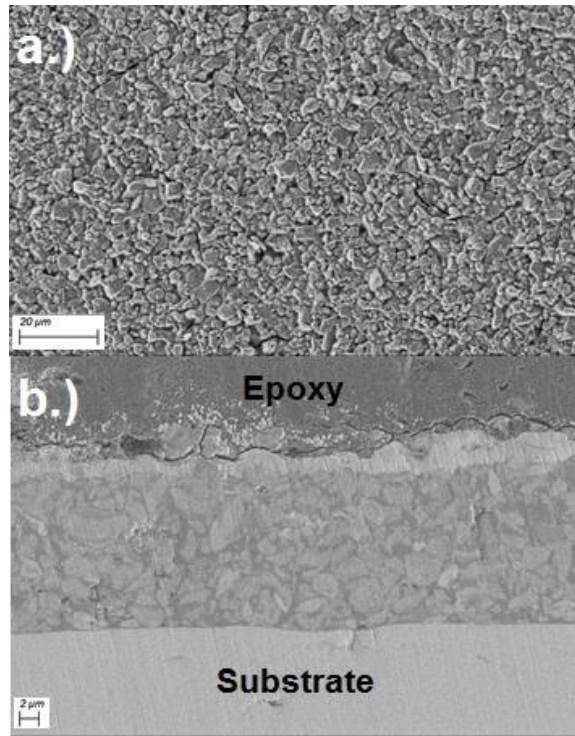


Figure 5.13. SEM (a) Plain-View and (b) Cross Sectional Image of 31% ZrSi_2 – PMHS [TYPE-2] Filler Composite after 600 °C Pyrolysis.

Figure 5.14 shows the TYPE-2 coatings ability to reduce oxide growth on Zircaloy-4 substrates when exposed to 800 °C ambient air conditions for 2, 5, and 10 hours. The theoretically calculated optimal filler volume of 31% for ZrSi_2 -PMHS systems was determined to be the best CMC composition for mitigating oxidation on the underlying substrate.

The TYPE-2 40% and 31% ZrSi_2 -PMHS coatings reduced oxide thickness (13.5 μm) by approximately 80% when exposed to 800 °C air for 5 hours. However, the 20% ZrSi_2 -PMHS coating showed significantly worse oxidation protection, even after only 5 hours. This is due to “through cracking” in the coating. This phenomenon will be further discussed in this section.

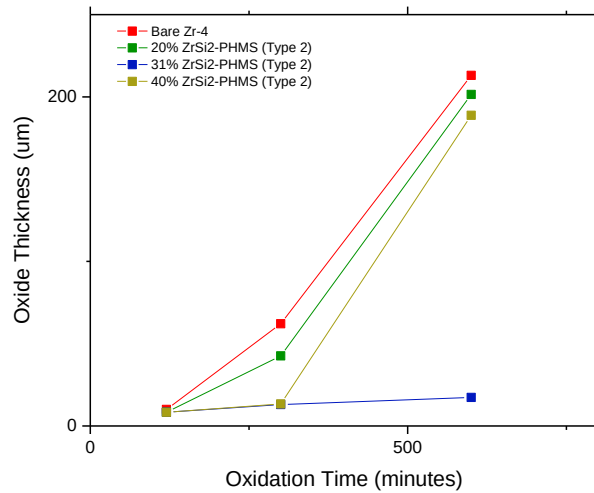


Figure 5.14. Oxide Growth Thickness for [TYPE-2] ZrSi₂-PMHS Composites at 800 °C for 2, 5, and 10 Hours Ambient Air Exposure.

After 10 hours exposure to 800 °C air, the TYPE-2 40% and 20% ZrSi₂-PMHS coatings were found to be significantly worse at mitigating the oxidation of the underlying Zircaloy-4 substrates. Whereas, the TYPE-2 31% ZrSi₂-PMHS coating showed significantly better oxidation protection [compared to bare Zircaloy-4] with an oxide thickness reduction of 92% (17 μm) after 10 hours of exposure. Figure 5.15 shows a comparison between bare Zircaloy-4, which had an oxide thickness of approximately 213 μm, and the TYPE-2 31% ZrSi₂-PMHS CMC coating. This is a significantly better protection compared to the TYPE-1 31% ZrSi₂-PMHS coating, which allowed an oxide growth of nearly 100 μm after 10 hours exposure. One interesting effect observed on the TYPE-2 31% ZrSi₂-PMHS CMC coating was in the “lipping” area. The substrate at the “lipping” location was subjected to a significant oxide growth due to large lipping induced through cracks leading to an oxide layer of ~ 180 μm (only 15% reduction to bare Zircaloy-4). This was clearly due to the “lip” formation since the cracking and oxide growth was extremely localized to this area of the substrate.

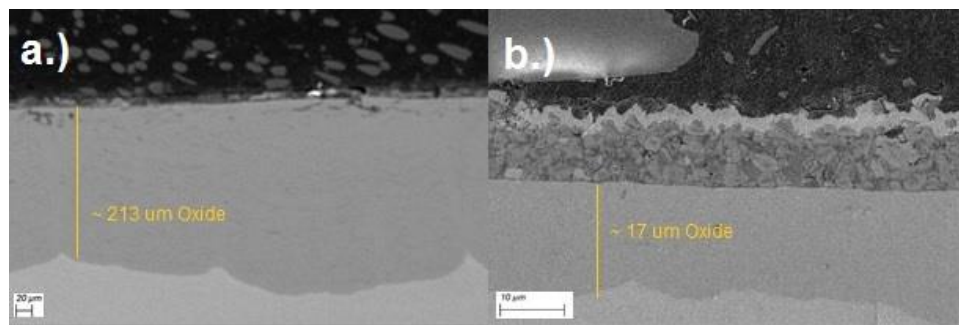


Figure 5.15. SEM Cross Sectional Images of (a) Bare Zircaloy-4 and (b) 31% ZrSi₂ – PMHS [TYPE-2] Filler Composite after Exposure to 800 °C Ambient Air for 10 Hours.

5.2.2. Addition of ZrO₂ in the ZrSi₂ Slurry Coatings

The use of additional inert ZrO_2 filler particles was explored to develop mixed filler zirconium silicide CMCs. Unlike ZrSi_2 , ZrO_2 particles are inert in oxidative environments and do not undergo volume expansion during exposure. Therefore, it is a suitable replacement for some of the SiOC matrix binder component. Using an additional 5 or 10 vol.% of the inert filler, the CMC was explored for its comparable oxidation protection and mechanical integrity properties as compared to 31% ZrSi_2 -PMHS coatings. The ZrO_2 particles were attrition milled in a basic deionized water (pH ~9) medium to nanometer scale with a maximum particle size of ~1 μm .

Figure 5.16 shows the resulting cross-sectional image of the 31% ZrSi_2 + 10% ZrO_2 – PMHS mixed filler TYPE-2 coating. The addition of inert filler particles to the suspension fluid precursor showed a highly homogeneous, low porosity ceramic product. The ZrO_2 particles can be observed in Figure 60 as the lighter particles, most of which are significantly smaller than one micron and highly dispersed throughout the composite matrix.

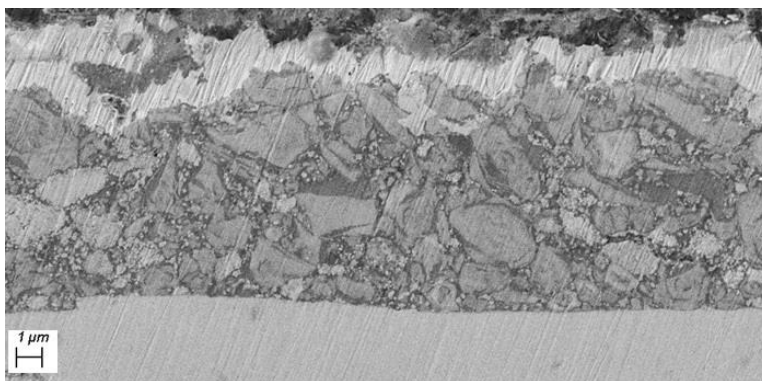


Figure 5.16. SEM Cross Sectional Image of 31% ZrSi_2 + 10% ZrO_2 – PMHS [TYPE-2] Mixed Filler Composite after 600 °C Pyrolysis.

5.2.3. Longer Oxidation of Slurry Coatings on Inconel 718

To investigate that the through-crack formation for the TYPE-2 ZrSi_2 -PMHS coatings on Zircaloy-4 was induced by the formation of a “critical oxide thickness”, samples were subject to significantly longer exposures at 800 °C in ambient air on an oxidation resistant substrate (Inconel 718). The coated sample was exposure to 800 °C in ambient air conditions for 100 hours. The extended exposure at harsh conditions were used to investigate whether through-cracks for formed due to significant degradation or confirm the theory that they are caused by internal stress from oxide growth. The resulting TYPE-2 ceramic coatings did not have any significant spallation or delamination after exposure but the TYPE-1 40% ZrSi_2 -PMHS coated sample had significant spallation (Figure 5.17).

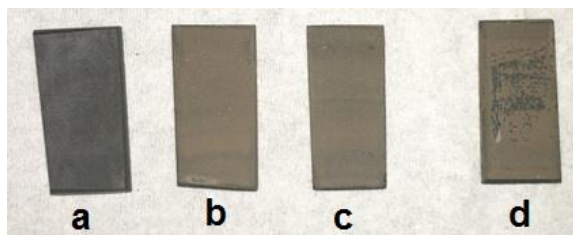


Figure 5.17. Photograph of 800 °C for 100 Hours in Ambient Air Exposure (a) Bare Inconel 718, (b) [TYPE-2] 40% ZrSi_2 -PMHS, (c) [TYPE-2] 30% ZrSi_2 -PMHS and (d) [TYPE-1] 40% ZrSi_2 -PMHS.

Exposure to 800 °C ambient air for 100 hours caused significant matrix shrinkage and filler particle oxidation resulting in a particle deformation, very high surface roughness, and an extremely hard ceramic product. The Inconel-718 substrates produced an oxide layer of approximately 1 micron. The thin oxide layer enabled us to ascertain the validity of the “critical oxide thickness” theory discussed previously.

The formation of large “through cracks” was not discovered in either TYPE-2 40% ZrSi₂-PMHS or TYPE-2 31% ZrSi₂-PMHS coated samples. This discovery enabled us to conclude that the “through cracks” for TYPE-2 composite coatings on Zircaloy-4 was a result from reaching a “critical oxide layer thickness”. Which, when reached, compromised the coating integrity as a viable oxidation barrier.

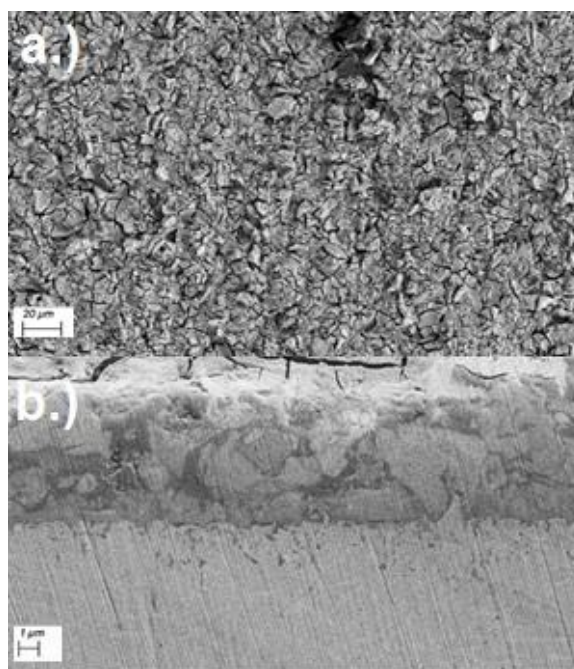


Figure 5.18. SEM (a) Surface Plain-View and (b) Cross Sectional Images of 31% ZrSi₂ – PMHS [TYPE-2] Filler Composite after 800 °C for 100 Hours in Ambient Air Exposure.

There was also evidence of a thin oxide layer formed on the Inconel 718 substrates. The oxide growth on the Inconel samples showed diffuse product mixing from sites in the substrate near the substrate-coating interface. The growth of the diffuse oxide mixing at the interface has been observed as a mechanism for supporting coating adherence at the interface of the substrate. The oxide layer, which was approximately 1 μm thick, was a result of a large amount of chromium diffusion from the substrate into the Si-O-C matrix at the coating-substrate interface. The mixing of the Si-O-Cr along the diffusion layer interface led to a strongly adherent bonding layer for the Inconel-718 samples. The Si-O-Cr diffusion bonding layer was confirmed using EDS (Figure 5.19).

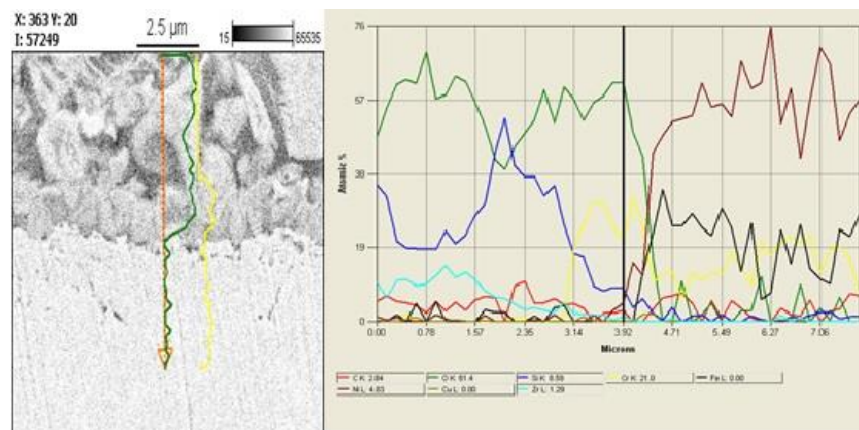


Figure 5.19. EDS Line Scan for Cross Sectional Image of 31% ZrSi_2 – PMHS [TYPE-2] Filler Composite TGO Bonding Layer Formed after 800 °C for 100 Hours in Ambient Air Exposure.

5.2.4. Steam Corrosion of Slurry Coating

Steam environment evaluations for zirconium silicide polymer derived ceramic coatings on Zircalloy-4 substrates were conducted to simulate harsh LWR systems. Since TYPE-2 CMC coatings showed a higher density, homogeneity, and reduced porosity, TYPE-2 coatings were determined to be the best possible coatings for steam environment testing and evaluations. The samples were mounted onto a nickel based support (Figure 5.20) and electrically isolated using alumina washers during mounting. The samples were loaded into high pressure/high temperature capable autoclave then subjected to 400 °C steam at 1500 psi for 72 hours.

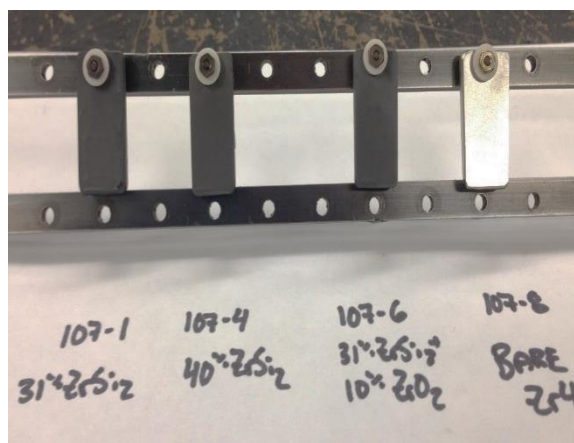


Figure 5.20. Photograph of Mounted Sample and Apparatus before High Pressure/High Temperature Steam Exposure.

High temperature, high pressure steam exposure resulted in significant coating failure for all TYPE-2 CMC coatings. The TYPE-2 40% ZrSi_2 -PMHS and TYPE-2 31% ZrSi_2 + 10% ZrO_2 -PMHS coatings had complete erosion after 72 hours. The TYPE-2 31% ZrSi_2 -PMHS was the only coating that was not completely eroded. However, remaining coating was significantly weaker, had significant spallation and could be easily removed after exposure.

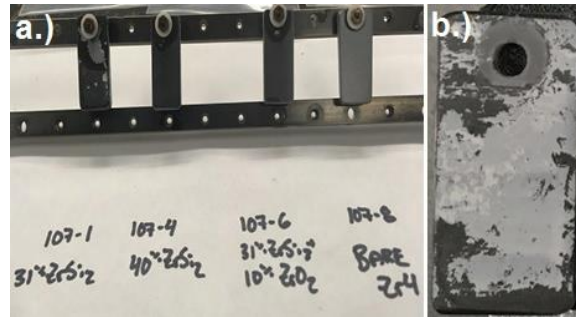


Figure 5.21. Photograph of (a) Mounted Sample and Apparatus and (b) Back Side of [TYPE-2] 31%ZrSi₂-PMHS Sample after High pressure/High Temperature Steam Exposure

Figure 5.22 shows a comparison of before and after high temperature and pressure steam for the TYPE-2 31%ZrSi₂-PMHS coating. Before steam exposure the coating surface has a clear SiOC matrix layer encapsulating the CMC and is extremely flat. In comparison, the coating surface is completely removed upon exposure to high temperature and pressure steam. This resulted in exposure filler particles and severe coating deformation (waves, bumps, cracks, etc.). From the SEM images in Figure 5.22, it can be hypothesized that the degradation occurred at the filler particle – SiOC matrix interfaces. This preferential corrosion likely led to the destabilization and removal of the filler particles resulting in a higher corrosion rate due to matrix embrittlement and more exposed SiOC surface area.

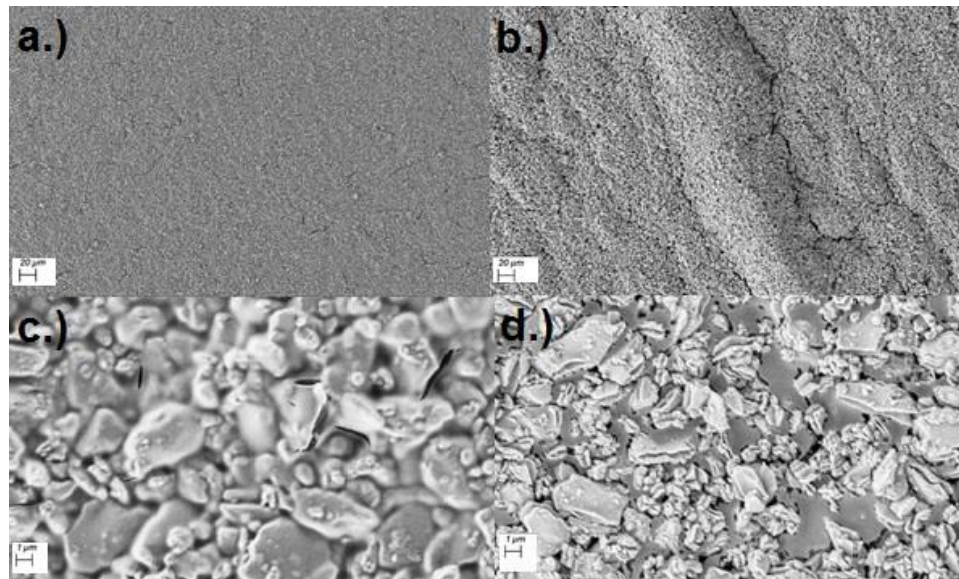


Figure 5.22. SEM Plain-View Image of [TYPE-2] 31%ZrSi₂-PMHS Coated Zircaloy-4 (a) and (c) before, (b) and (d) after High Pressure/High Temperature Steam Exposure.

5.3. Mechanical Integrity of Slurry Coatings

5.3.1. Micro-indentation test

To understand the mechanical integrity of the of the ZrSi₂ composites, the initial mechanical testing was performed on the particles themselves using a micro indenter on individual filler particles to evaluate the hardness of the filler component and its effects on the integrity of the slurry coating. The Vickers

hardness was measured for ZrSi_2 particles under a normal load of 0.5 gf and calculated by dividing the applied normal load (P) by the indentation area indicated by the indentation diagonal d_1 .

$$H_v = \frac{P}{A_1} = \frac{2P \sin(2\theta)}{d_1^2} \quad (\text{kgf mm}^{-2})$$

The Vickers hardness of the ZrSi_2 filler particles were averaged from five measurements and determined to be 59 GPa.

5.3.2. Scratch Test

Composites were also analyzed using a scratch test machine to evaluate the effects of filler particle size and volume under high loads on the scratch hardness of the composite coatings. For this method, samples were pyrolyzed at 600 °C on Zircalloy-4 prior to testing. Scratch tests were performed using diamond tipped scratch tester at a 15 mm/min traverse speed.

TYPE-1 (coarser filler) and TYPE-2 (finer filler) single filler samples were compared for 20%, 31%, and 40% ZrSi_2 filler volume. Each sample was evaluated using a scratch test with a 250g load. While the TYPE-2 samples had comparable trends to TYPE-1 samples, there was a significant reduction in crack propagation. The TYPE-2 samples showed a reduction in crack quantity and width (generally) and had a deeper and thinner scratch showing more shock or force absorption at the point of contact leading to less crack propagation. This increase in mechanical properties is advantageous for the integrity of the TYPE-2 coatings as potentially viable coatings. Figure 5.23 shows the direct comparison of filler particle size effects on the coatings mechanical integrity.

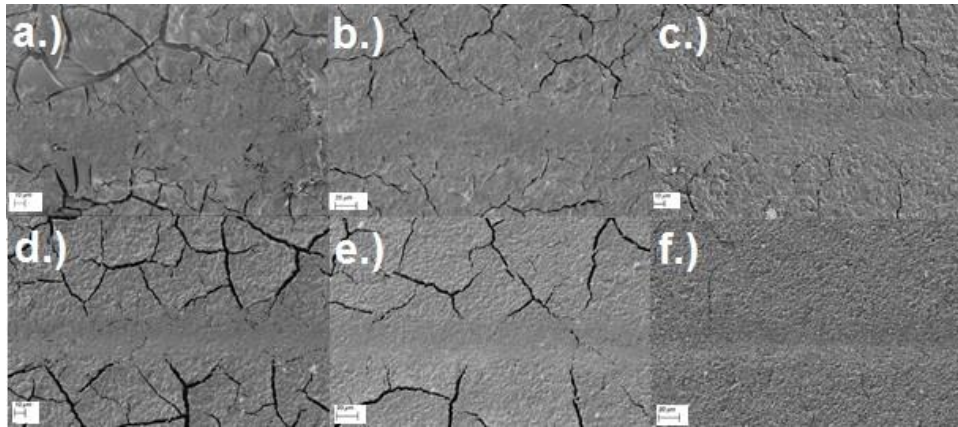


Figure 5.23. 250-gram Load Scratch Test Comparison for (a) & (d) 20% ZrSi_2 -PMHS and (b) & (e) 31% ZrSi_2 -PMHS and (c) & (f) 40% ZrSi_2 -PMHS TYPE-1 [Top] and TYPE-2 [Bottom] Composites.

The addition of a mixed filler to TYPE-2 composites were also investigated for a 250g load scratch test. The addition of 5% and 10% ZrO_2 submicron filler particles to the TYPE-2 31% ZrSi_2 -PMHS coating system shows a dramatic reduction in crack propagation. The mixed filler composite coatings were found to have wider indentation path widths but practically no crack propagation under a 250g load. The mechanical integrity against a surface impact is likely due to the more homogeneous and denser mixed filler coatings.

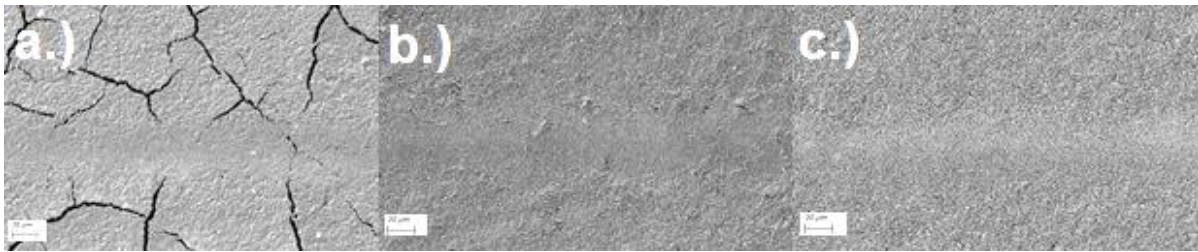


Figure 5.24. 250-gram Load Scratch Test Comparison for (a) 31% ZrSi₂-PMHS, (b) 31% ZrSi₂ +5%ZrO₂-PMHS and (c) 31% ZrSi₂ +10%ZrO₂-PMHS [TYPE-2] Composites.

5.3.3. Pin-on-disc Wear Track Test

The wear resistance of coatings on “soft” metals can be very advantageous in many industries. For Zircaloy-4 cladding, wear resistance for coatings is sought since wear on fuel cladding can be catastrophic and harmful. This is specifically of where the cladding interacts with the fuel assembly. This can potentially result in cladding failure or fuel leakage.

Initial wear tests were conducted on bare Zircaloy-4 and TYPE-2 40%ZrSi₂-PMHS coating samples using a ruby ball tip rotational wear tester with a track speed of 19.43 mm/min and track diameter of approximately 2.709 mm for 2 hours using a 1g load. There wasn't a significant wear effect under these conditions and required higher loading to produce a wear track that could be analyzed for comparability to Zircaloy-4.

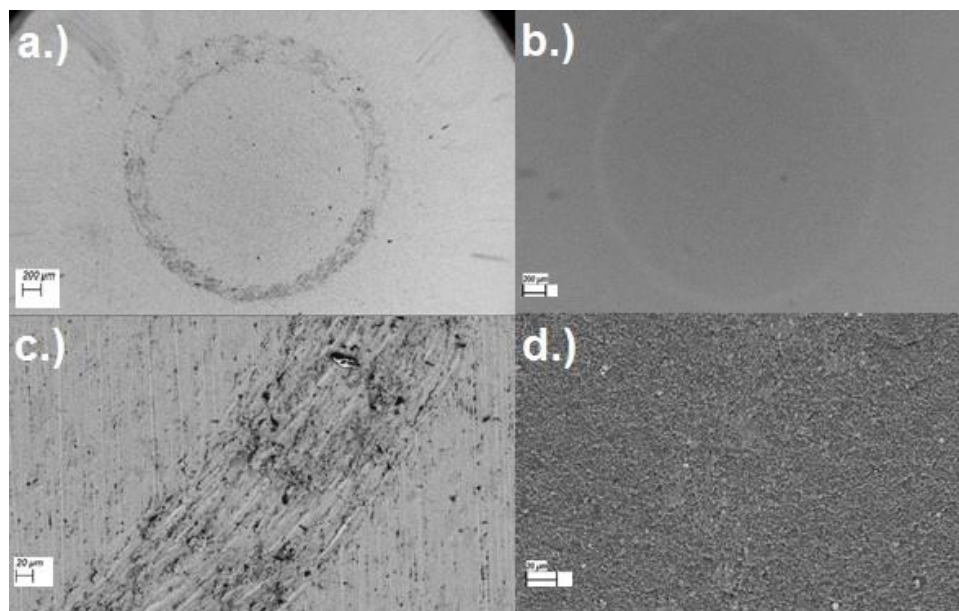


Figure 5.25. 1-gram Load Wear Test Comparison for (a) & (c) Bare Zircaloy-4 and (b) & (d) 40%ZrSi₂-PMHS [TYPE-2] Composite.

Figure 5.26 displays the comparison of wear tracks using a 100-gram load. The wear track width is drastically reduced for all coated samples evaluated compared to bare Zircaloy-4. The average wear track width for bare Zr-4 was determined to be approximately 964 µm. The greatest width reduction was in the TYPE-2 40%ZrSi₂-PMHS coating sample which had an average width of 172 µm. The TYPE-2 31%ZrSi₂-PMHS coating sample was severely worn after testing with nearly complete removal of the coating along

the wear track and significant cracking propagating from the wear track throughout the coating. An addition of 10% ZrO_2 to the TYPE-2 31% ZrSi_2 -PMHS coating resulted in a significant reduction in wearing along the wear track and a reduction of crack propagation from the wear location.

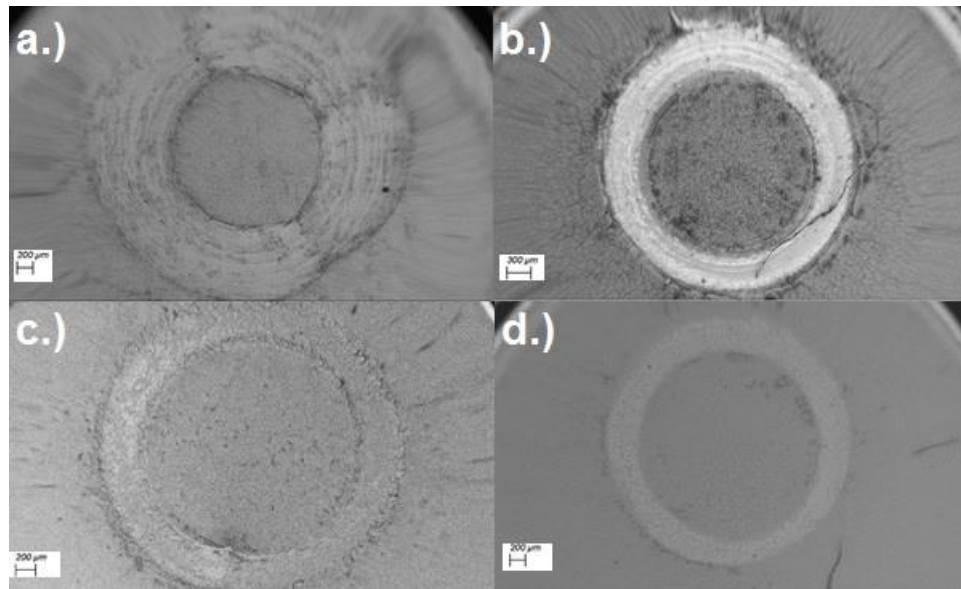


Figure 5.26. 100-gram Load Wear Test Comparison for (a) Bare Zircaloy-4, (b) 31% ZrSi_2 -PMHS, (c) 31% ZrSi_2 + 10% ZrO_2 -PMHS and (d) 40% ZrSi_2 -PMHS [TYPE-2] Composites.

Figure 5.27 displays higher magnification images for the wear tracks of the TYPE-2 samples and bare Zircaloy-4. The TYPE-2 31% ZrSi_2 -PMHS sample shows that after 2 hours of wear under a 100g load, the Zircaloy-4 substrate became exposed. The 31% ZrSi_2 + 10% ZrO_2 -PMHS and TYPE-2 40% ZrSi_2 -PMHS samples showed significant wear resistance. Wear testing on these samples resulted in the compression of coating along the wear track. The TYPE-2 40% ZrSi_2 -PMHS had the best wear resistance.

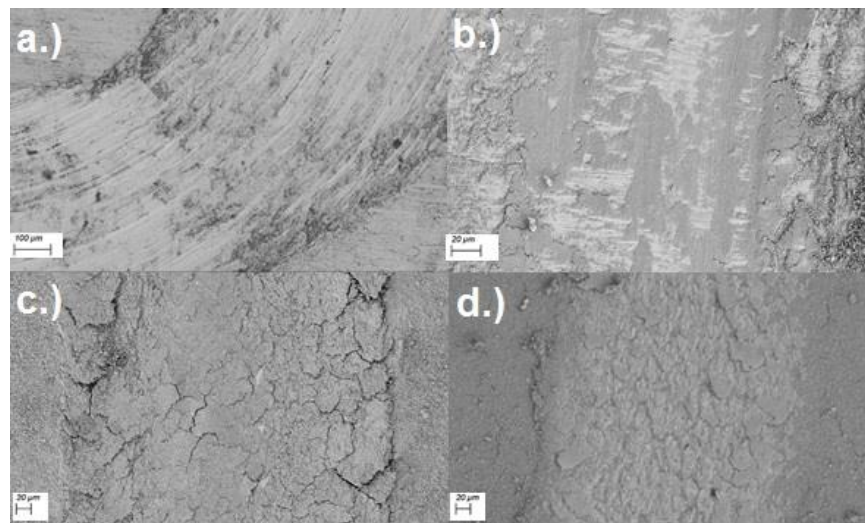


Figure 5.27. 100-gram Load Wear Track Comparison for (a) Bare Zircaloy-4, (b) 31% ZrSi_2 -PMHS, (c) 31% ZrSi_2 + 10% ZrO_2 -PMHS and (d) 40% ZrSi_2 -PMHS [TYPE-2] Composites.

Profilometry testing (Zygo) was performed to evaluate the wear rate of the coated samples and bare Zircaloy-4. Figure 5.28 shows a “heat map” with respect to surface height of each wear test. The line across the wear track for each test represents a series of cross-sectional data points used to extrapolate the wear area. The cross-sectional area for each wear test can be observed in the corresponding graph to each “heat map” in Figure 5.28.

$$\dot{W}_s = \frac{\Delta m}{\rho * F_N * L} = \frac{\Delta V}{F_N * L}$$

The wear rate can be calculated using the equation above, where ΔV is the wear track volume loss, F_N is the load force (Newtons), and L is the sliding distance. The volume loss in the wear track can be extrapolated from the circumference of the wear track and the cross-sectional area measured using the profilometry data in Figure 5.28. The sliding distance reference to the total distance traversed during the wear length of the wear test.

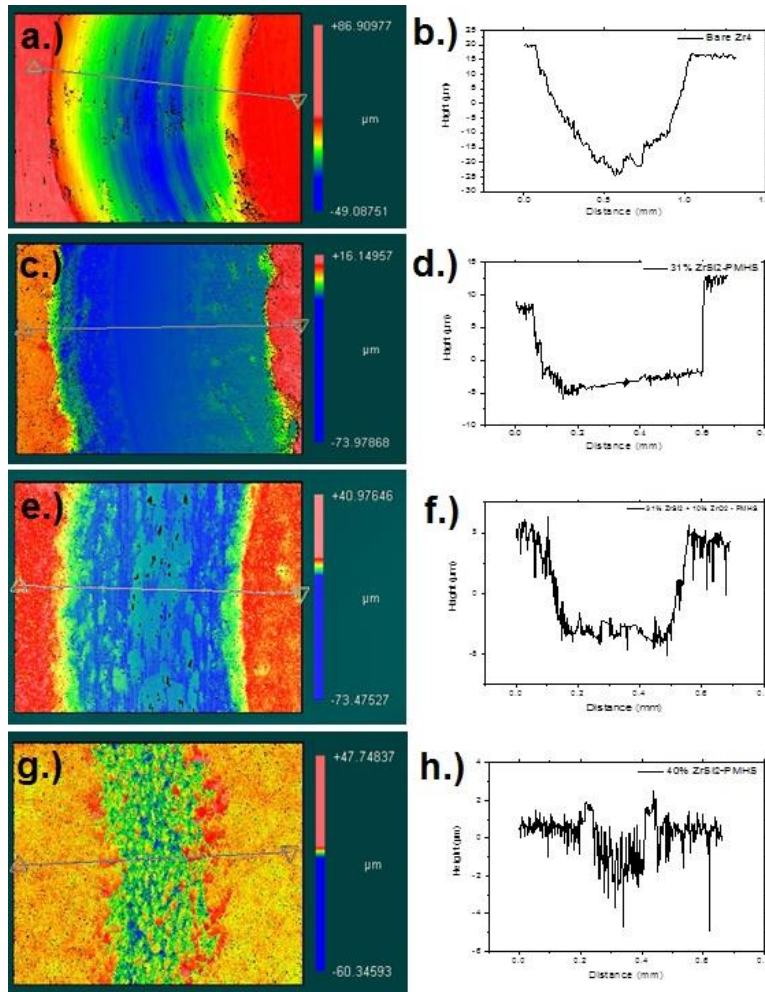


Figure 5.28. 100-gram Load Wear Profilometry Comparison for (a) & (b) Bare Zircalloy-4, (c) & (d) 31%ZrSi₂-PMHS, (e) & (f) 31% ZrSi₂ + 10%ZrO₂-PMHS and (g) & (h) 40%ZrSi₂-PMHS [TYPE-2] Composites.

The maximum depth of the wear track on the bare Zircalloy-4 substrate was determined to be 41.77 μm and the bare substrate showed a wear rate of 0.00155 mm³/Nm. These parameters were significantly

reduced using the zirconium silicide CMC coatings. The TYPE-2 2 40%ZrSi₂-PMHS was confirmed using the profilometry calculations to have the best wear resistance. The samples had a max track indentation depth of 5.37 μm , significantly less than the total coating thickness. The wear rate was also reduced by approximately 99%.

Table 5.2. 100-gram Load Wear Results Comparison for Bare Zircalloy-4, 31%ZrSi₂-PMHS, 31% ZrSi₂ +10%ZrO₂-PMHS and 40%ZrSi₂-PMHS [TYPE-2] Composites

	Bare Zircalloy-4	31%ZrSi₂-PMHS	31%ZrSi₂ + 5%ZrO₂-PMHS	40%ZrSi₂-PMHS
Max Depth (μm)	41.77	16.63	9.56	5.37
Cross Sectional Area (mm^2)	0.0255	0.00732	0.00307	0.000255
Volume Loss (mm^3)	0.2172	0.0623	0.0262	0.0022
Wear Rate (mm^3/Nm)	0.00155	4.452×10^{-4}	1.87×10^{-4}	1.55×10^{-5}

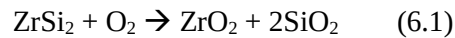
Chapter 6: Ion Irradiation of Oxidized ZrSi₂

This section introduces examining microstructural and compositional stability of oxide scales of ZrSi₂ (one of zirconium-silicide intermetallic compounds) under 3.9 MeV Si²⁺ ions at 305 °C. The oxidation of the bulk materials was performed at 1000 °C and 1400 °C in ambient air prior to the irradiation experiment. The oxidation of the material simulates material degradation at elevated temperatures by formation of surface oxide scale on zirconium-silicide structural components. Ion irradiation provided data on the radiation stability of these oxidized scales. In the paper, evolution of oxide phases of ZrSi₂ during the heat treatments was introduced first and radiation-induced phase alterations of the oxide scales was discussed. This study may provide initial experimental data and serve a better understanding of radiation response of zirconium-silicide in high temperature oxidative conditions.

6.1. Oxidation and Ion Irradiation

Polycrystalline and dense ZrSi₂ (American Elements Inc., Los Angeles, CA) with a reported purity of 99.5% was used in this study. All the samples were sectioned into dimension of approximately 5 mm × 10 mm, 6.4 mm thick square coupons. The mechanically polished specimens with 400 grit, 600 grit, and 1200 grit SiC abrasive papers were ultrasonic cleaned in acetone and ethanol bathes. Phase identification of the specimens using X-Ray Diffraction (XRD) and Scanning Electron Microscopy in conjunction with Energy Dispersive Spectroscopy (SEM-EDS) was reported in the previous literature [77]. Isothermal heat treatments of the as-polished specimens were performed at high temperatures using a commercial furnace (MTI Corp. Model GSL1600X). Different microstructures of oxide scale of ZrSi₂ specimens were prepared by oxidation at 1000 °C for 15 h and 1400 °C for 5 h in ambient air, respectively. Furnace ramp rate to the heat treatment temperature was kept at 5 °C/min.

Silicon irradiation for the oxidized ZrSi₂ samples was performed using the 1.7 MV tandem accelerator located at University of Wisconsin-Madison. 3.9 MeV Si²⁺ ions with 1.8×10^{17} ions/cm² dose was irradiated to obtain a high level of displacement damage. Focused beam normal to the sample surface scanned with vertical rate of 64 Hz and horizontal rate of 517 Hz. Sample temperature during the irradiation was 305 °C measured by two K-type thermocouples attached to a sample holder. The base pressure during the radiation was 3×10^{-7} torr. Fig. 6.1 shows estimated displacements per atom and concentration of implanted Si as a function of depth using the Monte Carlo simulation code SRIM-2013 [78] and the procedure described by Stoller et al [79]. Assumptions for sample geometry for the damage simulation in oxide layer at 1000 °C was homogeneous mixture of ZrO₂ and SiO₂ with a molar ratio of one to two (based on the oxide products in equation 6.1, Fig. 6.1a). Also, the dual-layered microstructure consisting of continuous ZrSiO₄ layer and SiO₂ was modeled in the SRIM code to simulate the two phases oxide scale which was previously reported in ZrSi₂ coating at 1400 °C (equation 2, Fig. 6.1b) [80].



Threshold displacement energies for Zr [81], Si [82], and O [83] were assumed to be 40 eV, 35 eV, and 23 eV, respectively. As shown in Fig. 6.1, the maximum damage in the oxide scale at 1000 °C and the oxide layer at 1400 °C was 61.7 dpa (2.16 μm in depth) and 64.5 dpa (2.31 μm in depth), respectively. Significant alteration of stoichiometry of the samples was not expected after the irradiation run because the maximum concentration of the implanted Si was about 5 at.% in both cases.

The irradiation effect on the surface morphology of the specimens was investigated by Zeiss LEO Scanning Electron Microscope in conjunction with Energy Dispersive Spectroscopy (SEM-EDS). Glancing-incidence XRD (Bruker D8 Discovery) was utilized for phase identification of the samples. Diffraction peaks from Cu Kα radiation were acquired from 30° to 50° in 2θ with a 2° grazing incident beam. Detailed

cross-sectional examination of the irradiated samples and the as-oxidized samples was performed with Transmission Electron Microscopes (TEM). A thin lamella was fabricated from the irradiated and unirradiated sample surfaces using the conventional Focused Ion Beam (FIB) technique. A thin Pt layer was deposited on the sample surface to protect the microstructure underneath the surfaces prior to the FIB cutting. The structural analysis and compositional characterization of the samples were conducted using Tecnai TF30 TEM operating at 300 kV and FEI Titan Scanning transmission electron microscope equipped with EDS (STEM-EDS) working at 200 kV. Table 6.1 summarizes experimental conditions of the samples in this study.

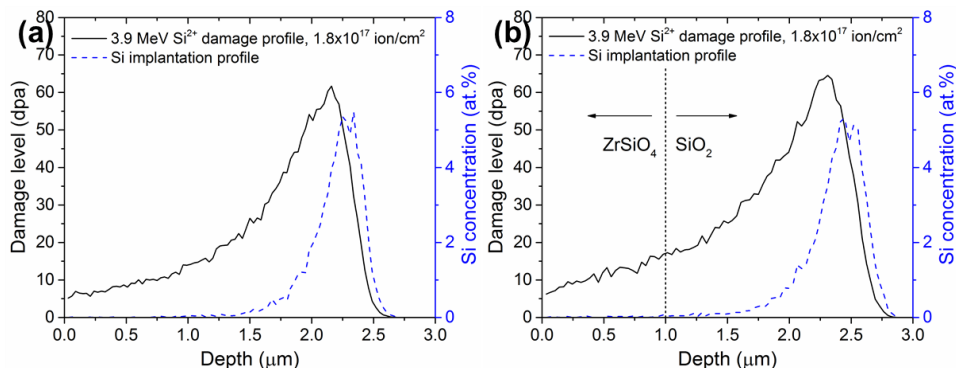


Figure 6.1. Depth profile of damage level (dpa) and implanted Si atoms in irradiated hypothesized oxide scales (a) homogeneous mixture of ZrO_2 and 2SiO_2 at 1000 °C and (b) dual-layer of ZrSiO_4 and SiO_2 at 1400 °C with 3.9 MeV Si ions. Calculations were performed using SRIM-2013 code.

Table 6.1. Summary of experimental conditions of ZrSi_2 in this study.

Sample ID	Experimental conditions
Sample A	Oxidation at 1000 °C for 15 h in ambient air
Sample B	Oxidation at 1400 °C for 5 h in ambient air
Sample AR	Ion irradiation of Sample A
Sample BR	Ion irradiation of Sample B

6.2. Oxide Structure of ZrSi_2 at 1000 °C and 1400 °C

Oxidation products of ZrSi_2 at 1000 °C and 1400 °C were identified as a result of the grazing incident XRD analysis as shown in Fig. 6.2. The XRD peaks for oxide scale at 1000 °C solely correspond to zirconium oxide phases - monoclinic ZrO_2 (m- ZrO_2) and tetragonal ZrO_2 (t- ZrO_2). It appears that high temperature t- ZrO_2 was not fully converted to m- ZrO_2 when the sample cooled down to room temperature [84]. Absence of SiO_2 peaks indicated SiO_2 was amorphous. At 1400 °C, pronounced diffracted beam from tetragonal zircon (ZrSiO_4) were observed and the intensity of the ZrO_2 peaks was remarkably lower than that of 1000 °C. Appearance of zircon phases (ZrSiO_4) at the high temperature (i.e. 1400 °C) indicates that formation of crystalline zircon phase is kinetically limited process even if it is thermodynamically favorable [85]. In other words, oxidation process at 1000 °C producing ZrO_2 and SiO_2 (equation 6.1) is a transition step prior to completion of oxidation of ZrSi_2 producing ZrSiO_4 (equation 6.2).

The surface morphology and chemical composition of the oxidized samples are shown in Fig. 6.3a and 3b. At 1000 °C, the surface was oxidized while maintaining the ratio of zirconium-to-silicon concentration similar to that of pristine ZrSi_2 . Fine oxide particulates emerged on the surface but it was too small to be quantified in the SEM image. Fig. 6.2b reveals the well-defined zircon grains on the oxidized surface at 1400 °C. Confirmation of zircon phase on the surface was performed by the XRD analysis and the EDS result; atomic percentage of zirconium equals to that of silicon on the surface. The zircon grain appeared to

be equiaxed in shape, in a couple of micron size, which embedded in darker matrix (i.e. SiO_2 rich phase – will be discussed in later). The cross-sectional SEM image of Sample A (Fig. 6.3c) shows complex nano/micro- structures consisting of fine and irregular ZrO_2 features and wavy SiO_2 matrix, which is consistent with the microstructure of oxide scale of ZrSi_2 at 1200 °C 5h [77]. The oxide scale of Sample B produced distinct layers ZrSiO_4 and SiO_2 as shown in Fig. 6.3d. Underneath the SiO_2 layer, reaction areas were mixtures of ZrSiO_4 , ZrO_2 , and SiO_2 , which was in good agreement with a proposed model for zircon formation by a solid-state reaction of t- ZrO_2 and amorphous SiO_2 [50]. An important observation was the oxide scale thickness at 1400 °C for 5h (about 32 μm) was thinner than that of 1200 °C 5 h (about 37 μm), which is contradicted to the general idea that oxidation rate is exponentially proportional to temperature. The thinner oxide scale at the higher temperature is attributable to the formation of oxidation resistant ZrSiO_4 layer in outer surface of the oxide scale. No spallation and delamination of the oxide scales were observed.

Figure 6.2. X-ray diffraction pattern of (red line) Sample A and (black line) Sample B with 2° incident beam.

Figure 6.3. Plan-view SEM images of (a) Sample A and (b) Sample B. The images were taken using 3 kV accelerating voltage. Atomic percent of zirconium, silicon, and oxygen on the surface is stated on each figure, measured by EDS

area scan analysis (15 kV accelerating voltage used). Cross-sectional SEM images of (c) Sample A and (d) Sample B show complex oxide microstructure. Phase of the oxide scale is labeled in Fig. 6.3d based on EDS point scan analysis.

Sample surfaces, after ion-irradiation run, were characterized via STEM and TEM. Sample A showed uniformly dispersed ZrO_2 embedded in a surrounding matrix of SiO_2 as shown in Fig. 6.4a. The nanocrystalline ZrO_2 had a diameter range from 15 nm to 25 nm. The selective area electron diffraction (SAED) pattern indicated ZrO_2 phases were randomly oriented t- ZrO_2 and m- ZrO_2 . The nucleation and growth of ZrO_2 nanocrystals during ZrSi_2 oxidation was observed in 1200 °C for 5 h oxidation as well, which was explained by the extension of miscibility gap in the binary ZrO_2 and SiO_2 phase diagram [77]. Moreover, the rounded fine ZrO_2 grains dispersed in SiO_2 was also reported in annealing of highly damaged natural zircon at 1200 K for 16 h [86]. The dispersed nanocrystals in the oxide scale may introduce radiation defect sinks such as interphase surfaces and grain boundaries, leading to suppress potential radiation damage. The microstructure of Sample B consisted of polygonal zircon grains of a few micron size. SiO_2 phase around the grains was bright contrast in the ABF image of STEM (Fig. 6.4c). A couple of ZrO_2 rich particulates were inside the zircon grains, which is an indicative of incompleteness of zircon formation through the solid-state reaction of ZrO_2 and SiO_2 . In addition, the image reveals dislocations inside the zircon grains. The SAD patterns from a zircon grain show single crystal tetragonal ZrSiO_4 . SiO_2 turned out to be amorphous as shown in Fig. 6.4d.

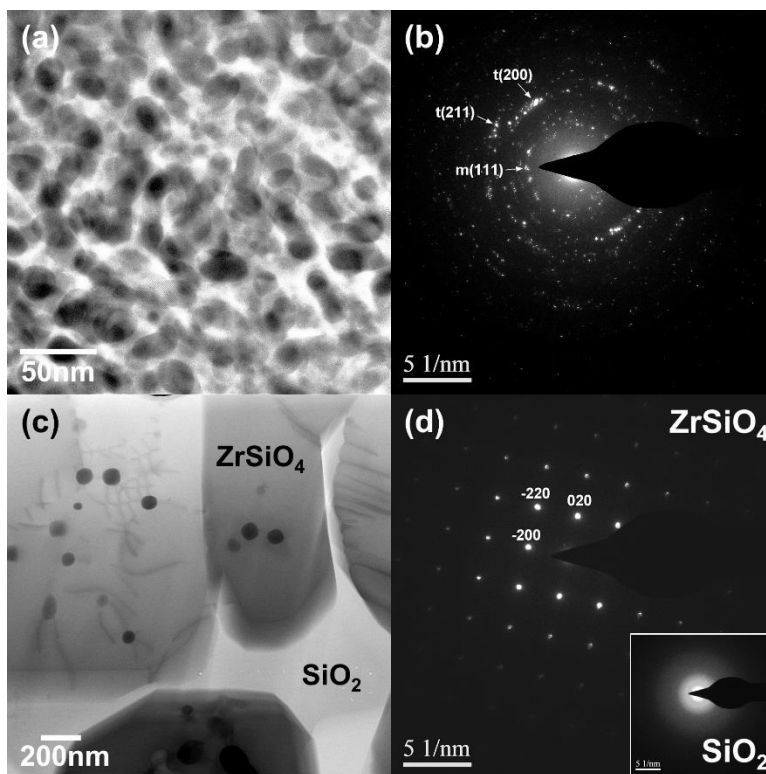


Figure 6.4. STEM annular bright field images and TEM selected area electron diffraction (SAED) patterns of near surface of (a, b) Sample A and (c, d) Sample B. The inset in Fig. 6.4d shows amorphous fuzzy ring in the SiO_2 phase. Distinct features of the oxide scales with different temperatures are displayed and the diffraction patterns were labeled.

6.3. Characterization of irradiated oxide scale of ZrSi_2

Radiation response of the oxide scales was characterized by glancing-angle XRD as shown in Fig. 6.5. In Sample AR irradiated with 1.8×10^{17} ion/cm² dose, two types of ZrO_2 peaks were pronounced similar to

the un-irradiated specimen. However, in Sample BR the tetragonal zircon phases were heavily damaged so that intensity of the diffracted peaks shown in Fig. 6.2 significantly were decreased. It is a clear indication of irradiation-induced crystalline-to-amorphous transformation in zircon grains.

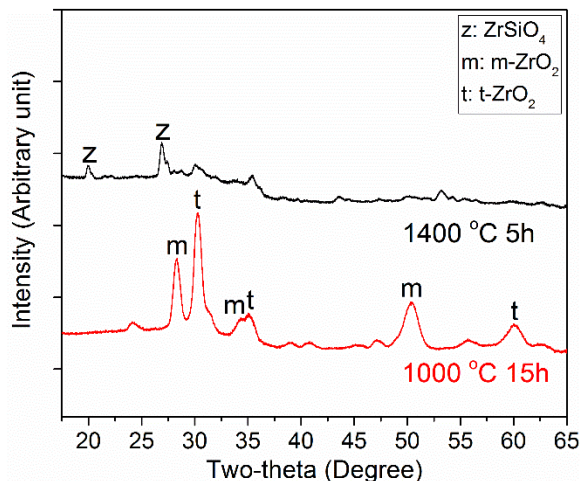


Figure 6.5. X-ray diffraction pattern of ion-irradiated (red line) Sample AR and (black line) Sample BR with 2° incident beam.

SEM images of surface morphology on the oxidized ZrSi_2 after the radiation exposure is given in Fig. 6.6. The irradiated surfaces showed fine and uniform textures. Surface on Sample AR revealed periodic ripple pattern with a characteristic wavelength of about one micron. On surface of Sample BR, the surface topography revealing zircon grains became very obscure as shown in Fig. 6.6b. The individual zircon grains were difficult to distinguish in the image. It is believed that the surface modifications were caused by interplay between sputtering-induced surface roughening and surface relaxation via radiation-assisted viscous flow and diffusion [87]. Similar trend was mainly observed in amorphous materials like SiO_2 which is main component in the oxide scales of ZrSi_2 . The average EDS data on $60 \mu\text{m} \times 70 \mu\text{m}$ surface area shows that oxygen concentration was slightly increased on both conditions possibly due to participation of residual oxygen in the environment into the surfaces via radiation-enhanced diffusion. The increase in Si concentration on the surface (Fig. 6.6b) is attributable to phase mixing or radiation-induced deformation of SiO_2 phase (enhanced mobility under the irradiation) which was originally located underneath the ZrSiO_4 grains.

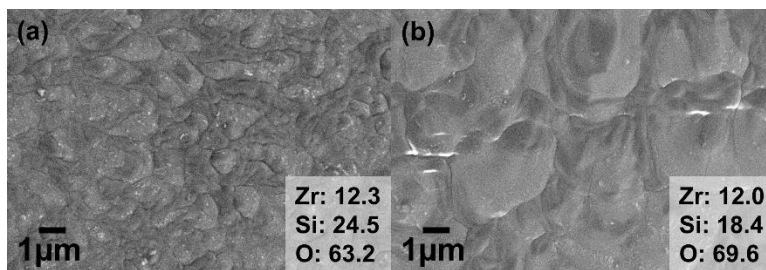


Figure 6.6. SEM surface morphologies of ion-irradiated samples – (a) Sample AR and (b) Sample BR. The images were acquired with 3 kV accelerating voltage. Atomic percent of zirconium, silicon, and oxygen on the surface is specified on each figure, measured by EDS area scan analysis.

The thin lamella fabricated from surface of the irradiated Sample AR was examined by STEM-EDS and TEM. High-Angle Annular Dark Field (HAADF) images of Sample AR with low magnification is shown in Fig. 6.7a. The contrast of the images is sensitive to variations in atomic number of atoms in the

sample; the brighter species in HAADF image contain higher zirconium concentration. Nanocrystalline ZrO_2 spherical phases largely disappeared close to the sample surface. However, the complex oxide microstructure revealed again in the depth of ~ 820 nm. It means that the structural transformation (i.e. phase mixing) of the ZrO_2 - SiO_2 nanocomposite occurred as a result of radiation damage. It is worth noting that the ion-mixing was not fully completed in the heavily damaged region as the high magnification ABF-STEM image (Fig. 6.7b) still displayed darker contrast ZrO_2 . The SAED pattern taken near the sample surface shows amorphous ring with weak t- ZrO_2 spots, supporting the substantial amorphization and phase mixing of the oxide scale. Amorphization phenomenon in ceramics is considered as an ion-assisted solid-state inter-diffusion reaction but the degree of the amorphization was not uniform in the damaged area. Higher intensity and more number of the crystalline diffraction spots were revealed in the diffraction pattern in the depth of ~ 350 nm (damage level was 7.4 dpa) from the surface even where is still in the high dose region. Finally, strong diffraction spots corresponding to m- ZrO_2 and t- ZrO_2 were recognized in the SAED pattern in the depth of 1.35 μm . The complex oxide structure preserved even though irradiation damage was very high (i.e. 20.6 dpa) at this area. The interesting result will be discussed further in Discussion section.

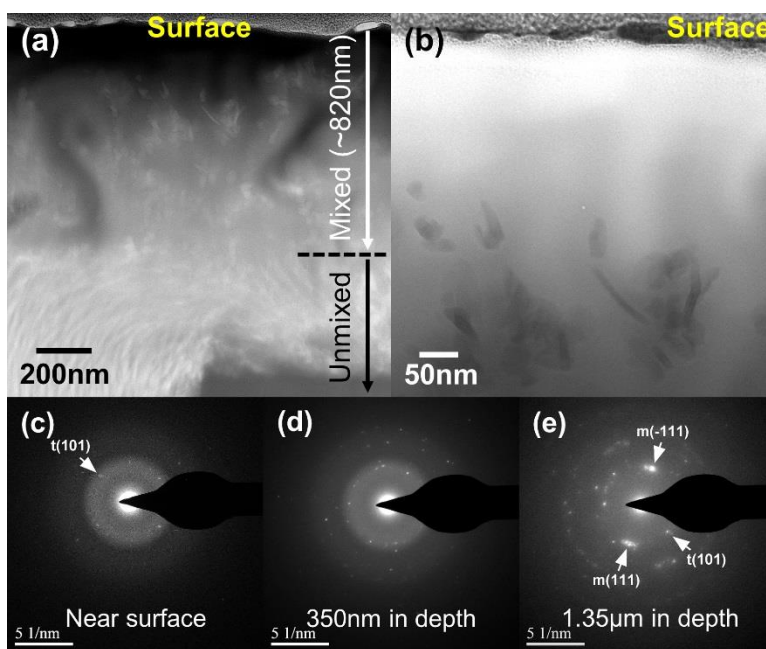


Figure 6.7. (a) High Angle Annular Dark Field (HAADF) STEM cross-sectional image near the surface of Sample AR at low magnification. The intensity of the images increases with atomic number. (b) ABF STEM image with high magnification. (c-e) SAED patterns in Sample AR at different depths from the surface.

The ion-beam-mixing effect is evidently observed in comparison of two STEM-EDS line profiles (Fig. 6.8) acquired at ~ 350 nm in depth from the sample surfaces. The ZrO_2 nanocrystals with width of tens of nanometers were uniformly distributed along with SiO_2 phase in the un-irradiated oxide scale (Sample A). The microstructure is responsible for the alternating elemental composition between zirconium and silicon in the EDS result (Fig. 6.8b). The compositional wavelength was approximately 40 nm. However, radiation-induced phase mixing led to disappearance of sharp interface between ZrO_2 and SiO_2 . The STEM-HAADF image of Sample AR (Fig. 6.8c) shows a small number of brighter grains (enriched in Zr) in darker contrast Si-rich matrix. Based on the EDS analysis, the chemical composition of both zirconium and silicon was levelled out, which is a strong indication of a homogenous mixing of the fine ZrO_2 and SiO_2 phases. Interestingly, bulk ZrO_2 is known as highly radiation resistant material. Sickafus et al. [88] reported that

bulk m-ZrO₂ resisted radiation-induced amorphization after Xe²⁺ ions irradiation from 170 K to 300 K up to a peak damage level of 680 dpa. Instead, m-ZrO₂ was transformed to high temperature metastable phases, tetragonal or cubic phases. Similar to the present study, however, Meldrum et al. [89] observed that 1.0 MeV Xe²⁺ ion irradiation caused amorphization of nanocrystalline ZrO₂ (3 nm-diameter) in amorphous SiO₂ matrix at a dose of 0.9 dpa and room temperature. The authors hypothesized that ion-irradiation could increase total free energy of nanocrystal ZrO₂ of a large surface energy sufficiently higher than bulk ZrO₂ so that amorphous ZrO₂ may be produced. Therefore, the phase mixing in Sample AR could be also explained by the thermodynamic approach.

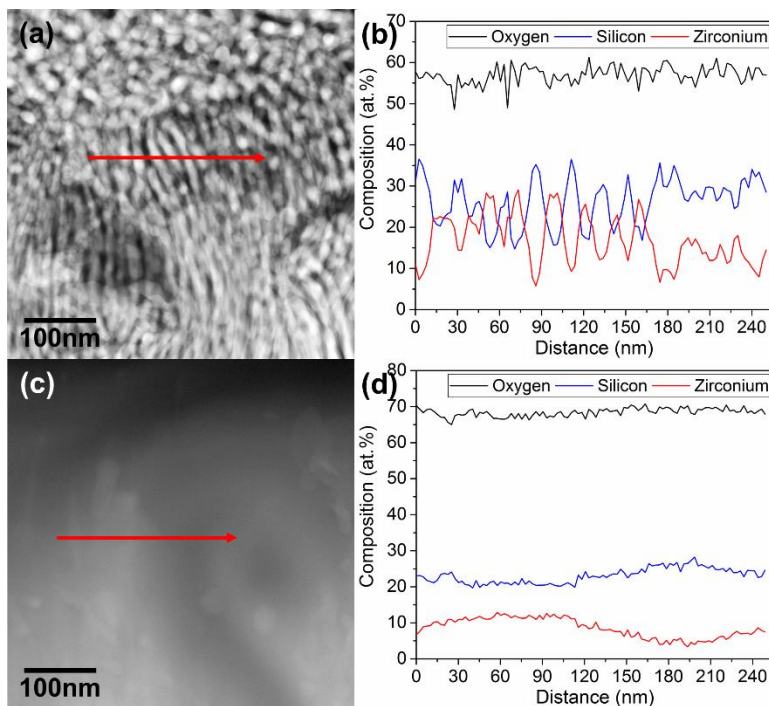


Figure 6.8. HAADF STEM images and figures of composition of zirconium, silicon, and oxygen obtained by EDS line scan for (a, b) un-irradiated Sample A and (c, d) irradiated Sample AR. The images were taken at 350 nm in depth from the sample surface. The red arrows indicate the EDS line scan path.

As shown in bright field TEM image (Fig. 6.9a), the irradiated cross-section Sample BR showed a sharp transition near the damaged region boundary estimated by the SRIM calculation (Fig. 6.1b). Crystallinity of zircon grains was lost in the radiation damaged region (up to $\sim 2.9 \mu\text{m}$ depth). The damaged region did not reveal polygonal zircon grains anymore. Instead, irregular morphology was observed as a response to the ion irradiation. Near the sample surface, smeared Zr-Si-O phase without grain boundaries was identified, as well as Si-rich phases (the dark phases indicated by the red arrow in Fig. 6.9b) nearly perpendicular to the incident beam. It appears SiO₂ rich phases originally existed between the zircon grains as shown in Fig. 6.3b and Fig. 6.10 viscously flowed. For example, under 4.0 MeV Xe⁴⁺ irradiation and room temperature, amorphous SiO₂ showed a dramatic macroscopic deformation that the silica expanded perpendicular to the ion beam direction [90]. The anisotropic deformation and enhanced plastic flow of SiO₂ was explained by local heating and thermal expansion by intense electronic excitation followed by rapid quenching [91]. In addition, some spherical ZrO₂ phase originally embedded in zircon grains remained intact after the radiation damage. The radiation-induced amorphization was confirmed by electron diffraction (Fig. 6.9c). Strong amorphous diffuse halo was revealed in the irradiated sample as deep as $2.6 \mu\text{m}$. On the other hand, some strong spots in selected-area electron diffraction pattern can be indexed as tetragonal ZrSiO₄ at undamaged region of the sample (Fig. 6.9e). According to the publish data using heavy ion-implantations (e.g. 0.8 MeV

Kr⁺ ions [92] and 0.3 MeV Pt⁺ ions [93]), ZrSiO₄ can be amorphized as low as ~ 0.43 dpa at room temperature. The critical amorphization dose at 305 °C showing a complete loss of crystallinity is approximately 0.6 dpa based on the amorphization/recrystallization model [94], which is still far below the current radiation dose. High irradiation temperature permits amorphous phase to recrystallization but full recovery of the structural disorder of ZrSiO₄ may require a large amount of thermal energy due to the large complex unit cells, and the narrow phase field (i.e. line compound).

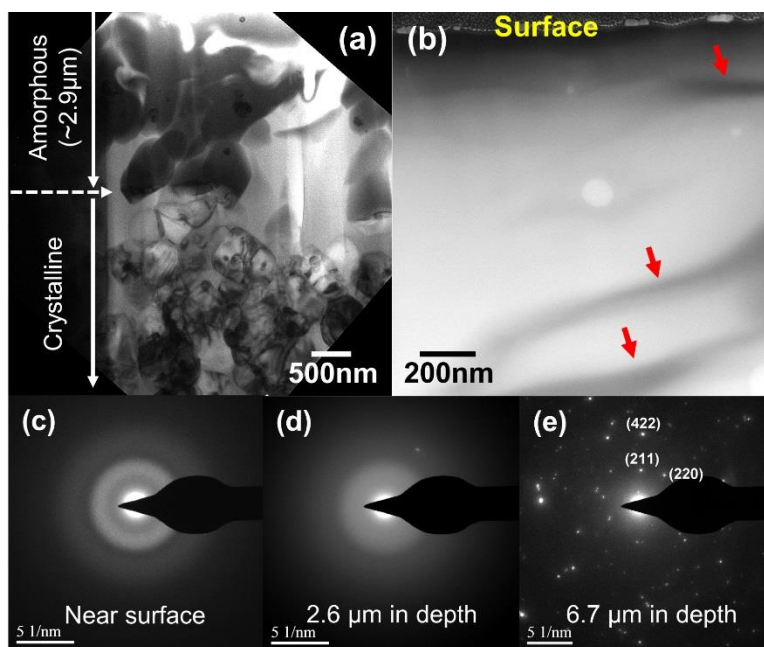


Figure 6.9. (a) low-magnification TEM image and (b) HAADF STEM image of cross-section of irradiated sample BR. Damaged depth (~2.9 μm) is indicated by white dash line in Fig. 6.9a and silicon-rich phases were pointed by the red arrows in Fig. 6.9b. (c-e) SAED patterns in Sample BR with different depth from the surface. Index of some diffraction spots in Fig. 6.9e match with tetragonal ZrSiO₄.

6.4. Radiation-Assisted Corrosion Resistance

Distinct material response of the oxide scales of ZrSi₂ (Sample AR and Sample BR) under Si ion irradiation can be summarized as morphological changes, phase mixing, and amorphization of the oxide phases. One important factor for application of the structural ceramic materials in extreme conditions is corrosion resistance in water vapor containing high temperature environments. Unfortunately, silicon based structural materials (e.g. Si₃N₄ and SiC) prone to experience weight loss and surface recession under high temperature water conditions [95]. Although passive SiO₂ layer forms on the surface in reaction with water and oxygen, dissolution of the SiO₂ phase in water would prevail due to enhanced solubility of SiO₂ [60] and volatility of SiO₂ [61] with increasing temperature and pressure. Furthermore, the corrosion rate can be accelerated if the material contained irradiation defects [96]. Hence, it is anticipated that water corrosion of Sample A would be facilitated by dissolution of the amorphous SiO₂ matrix in the oxide scale. Additionally, zircon formed from ZrSi₂ (Sample B) can immobilized silicon species in the oxide scale in water vapor environment but there would be preferential corrosion in grain boundaries. Ueno et al. [63] reported that corrosion of synthetic bulk ZrSiO₄ at 1300 °C static water vapor corrosion test was localized around the grain boundaries due to a significant amount of potential SiO₂ rich composition. As shown in Fig. 6.10, Si-rich region was identified between two zircon grains in Sample B where localized corrosion is expected when the oxide scale is exposed in high temperature aqueous conditions. Generally, hydrothermal corrosion

of ceramics initiates in grain boundary phases and dissolution of ceramic grains promoted water transport along the grain boundaries into the bulk material.

It is strongly believed that the structural homogeneity of the irradiated oxide scales may exhibit excellent corrosion resistance. The radiation damaged regions were structurally and chemically homogenous without distinct microstructure like grain boundaries which could act as local corrosion activation site. Particularly, the Si-rich phases between zircon grains in the zircon that underwent preferential corrosion were eliminated after the ion irradiation as shown in the SEM plan-view image (Fig. 6.6b). It is hypothesized that corrosion performance of the homogenous chemical mixture of zirconium-silicon-oxygen (Fig. 6.8c) is better than that of mixture of ZrO_2 and SiO_2 (Fig. 6.8a). The radiation-enhanced corrosion resistance should be investigated by performing high temperature water corrosion tests of the irradiated samples to examine the hypothesis.

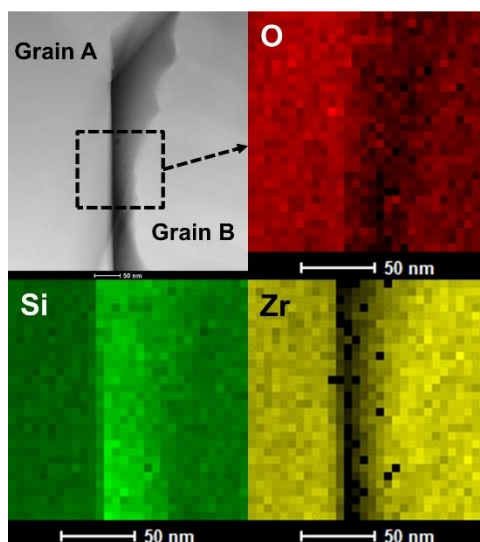


Figure 6.10. HAADF image of a grain boundary between two zircon grains and EDS maps for oxygen, silicon, and zirconium in Sample B.

Radiation-assisted phase mixing of Sample A was only observed at the limited depth of the radiation damaged region. Depth of the ion-mixing region was determined to be approximately 820 nm based on the TEM images even though the peak damage level (61.7 dpa) was estimated in 2.16 μm in depth. Nevertheless, the complex microstructure consisting of ZrO_2 and SiO_2 was maintained at the area of the maximum damage level. The controversial radiation response can be elucidated by effects of grain size of ZrO_2 on the phase transition. Interestingly, the microstructure of nanocomposite in Sample A evolved in different shapes in different depths as shown in the cross-sectional SEM image (Fig. 6.3c). Near the sample surface, the oxide scale contained fine spherical ZrO_2 phases in SiO_2 matrix as shown in Fig. 6.4a. Around 350 nm in depth of the sample, the ZrO_2 phases showed elongated features and the longer axis was perpendicular to the surface. At deeper region of the sample, dog-bone shaped ZrO_2 grains embedded in amorphous SiO_2 were identified as shown in Fig. 6.11a and the corresponding result of EDS line scan shows alternating composition of zirconium and silicon. The size of the ZrO_2 grains measured by ImageJ software as per ASTM E1382 [97] was summarized in Fig. 6.11c with the calculated damage level. Partial or complete amorphization of the smaller ZrO_2 grains (< 25 nm) in SiO_2 matrix was induced up to 11 dpa but larger ZrO_2 grains (25 nm to 50 nm) tolerated high radiation damage (up to 60 dpa). It is contradicted to general idea that the finer nanocomposite has a large fraction of solid-solid interfaces such as inter-phase boundaries and grain boundaries providing more chances to annihilate radiation defects. Shen [98] proposed that there were two competing effects of grain size on the radiation resistance of nanocomposite materials (the grain

size is less than 100 nm). First, concentration of point defects in irradiated grain is proportional to the grain size; excess of free energy of irradiation-induced point defects (ΔG_{pd}) tends to be lower in a smaller grain size (d). On the other hand, free energy of the material increases with decreasing grain size due to larger area fraction of grain boundaries (ΔG_{gb}). The qualitative trends were plotted in Fig. 6.12 based on the proposed formulations for the free energies under assumptions (e.g. defect annihilation is dominated by grain boundary sink). The author hypothesized that the phase transition (e.g. phase mixing) is thermodynamically available only when Gibbs free energy of the phase mixing (ΔG_{mix}) is lower than a sum of the two free energies as shown below:

$$\Delta G_{mix} < \Delta G_{pd} + \Delta G_{gb} \quad (6.3)$$

Based on the model, the small ZrO_2 nanocrystals (below 25 nm) near the surface were susceptible to the radiation-induced phase mixing due to a large ΔG_{gb} term; the grain size (d) is smaller than the critical grain size (d_{crit}) shown in Fig. 6.12. However, the larger grains (25 nm to 45 nm) in the damage region did not experience the phase transition due to a balance of the two free energy terms – there is a window for grain size showing phase mixing resistance (as described in equation 6.4) while increasing grain size in the range tends to increase ΔG_{pd} but the sum of the two excess free energies is smaller than ΔG_{mix} due to decrease in ΔG_{gb} .

$$\Delta G_{pd} + \Delta G_{gb} < \Delta G_{mix} \quad (6.4)$$

It is anticipated that radiation response of much larger ZrO_2 grains (> 100 nm) dispersed in SiO_2 is different from the nanocomposite. Instead of the phase mixing, the large grains might be transformed from m- ZrO_2 to high energy metastable t- ZrO_2 and c- ZrO_2 phases (ΔG_{tr}). It was estimated that the excess energy required for phase transformation from m- ZrO_2 to t- ZrO_2 was only one third of that for amorphization of m- ZrO_2 [99]. The total energy of the material dominated by formation of point defects cannot reach the energy of phase mixing (ΔG_{mix}) but is larger than the energy of the structural transformation (ΔG_{tr}). The energy state is described in equation 6.5. However, further experimental study needs to be performed to support this speculation.

$$\Delta G_{tr} < \Delta G_{pd} + \Delta G_{gb} < \Delta G_{mix} \quad (6.5)$$

In addition, it is worth it to note that the phase mixing was not observed in W/ ZrO_2 nanocomposite system with periodic bilayer thickness of (7/14 nm) under Au^+ ion irradiation [100]. It is assumed that the nanocomposite system has a positive heat of mixing and exhibits strong immiscible both in solid and liquid phases, resulting in suppression of phase-mixing. Since free energy of binary ZrO_2 - SiO_2 system could be minimal by forming $ZrSiO_4$ phase, however, the ΔG_{mix} term is presumed to be smaller than that of the immiscible nanocomposite system.

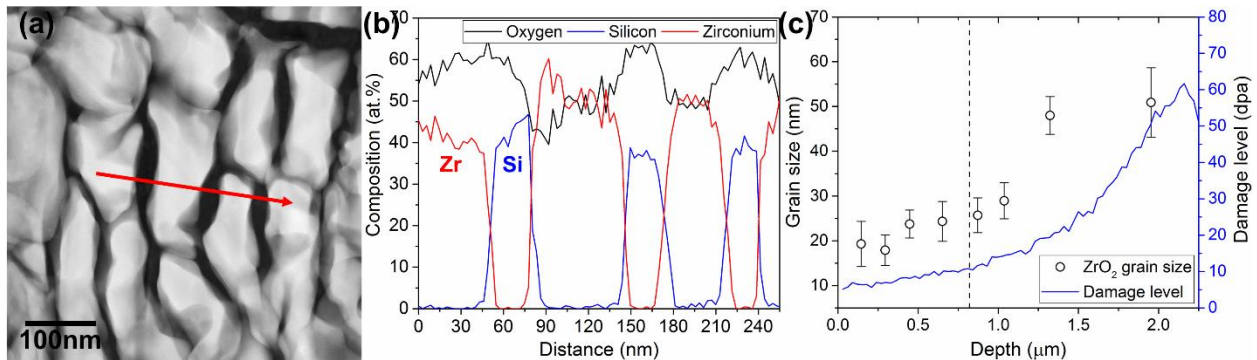


Figure 6.11. (a) HAADF STEM image and (b) composition of zirconium, silicon, and oxygen obtained by EDS line scan for un-irradiated Sample A. The images were taken at approximately 8 μm in depth from the sample surface. The

red arrows indicate the EDS line scan path. (c) depth-wise ZrO₂ grain size and damage level (shown in Fig. 6.1a). The grain sizes were measurements at four evenly spaced directions (0°, 45°, 90°, 135°) of each grain in STEM images of Sample A. The dark dots line indicates the measured ion-mixing interface (~ 820 nm).

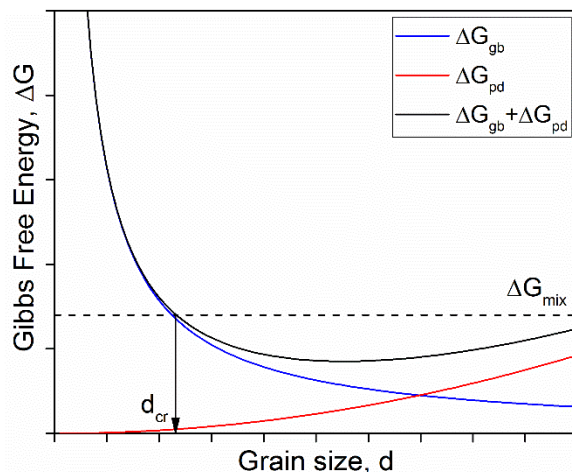


Figure 6.12 Schematic diagram of the Gibbs free energy of grain boundary (ΔG_{gb}), point defect (ΔG_{pd}), total energy ($\Delta G_{gb} + \Delta G_{pd}$), and phase mixing (ΔG_{mix}) as a function of grain size, based on Shen's model [98]. It proposes that phase mixing of ZrO₂ and SiO₂ is thermodynamically favorable if the grain size is smaller than the critical grain size (d_{cr}).

The present study shows that tenacious oxide scales of the zirconium-silicide formed at elevated temperatures provides engineering benefits as a structural material in oxidative and radiation environment. Radiation-induced corrosion/oxidation resistance is likely attained in the oxide scales due to microstructural homogeneity. Application of the findings is not limited to improvement of the current nuclear system (e.g. accident tolerant nuclear fuel coating) and to simulate degradation of the potential neutron reflector in advanced nuclear reactors. The nanocomposite layered zirconium-silicide or freestanding nanocomposite (produced by complete oxidation of ZrSi₂) could be an attractive structural material in future spacecraft applications, detectors, and sensors subjected to energetic ions environments. The study showed that Zr-Si-O system has two metastable phases and one stable state as follows: (i) amorphous Zr-Si-O, (ii) nanocomposite of ZrO₂ and SiO₂, and (iii) crystalline ZrSiO₄. Transition between the states can be available by external energy inputs such as thermal energy (become more stable phase) and irradiation energy (transition to metastable phase).

Chapter 7: Quenching Heat Transfer of Sputter ZrSi₂ Coatings

Thin ZrSi₂ coatings were deposited on cylindrical Zircaloy-4 rodlets, and transient boiling heat transfer during a rapid quenching under saturated, subcooled, and pressurized water conditions were explored. Temperature history at a center of the test section was measured and boiling visualization was performed during the quenching experiments. Coating damage effects such as cracking, delamination, and surface oxidation during the rapid quenching were characterized, and effect of the ZrSi₂ coating on quenching performance is discussed in detail. This type of test simulates activation of emergency core cooling system (ECCS) injection in accident scenario.

7.1. Coating Deposition and Quenching Facility

The zirconium-silicide coatings were deposited on Zirc-4 flats, SiC flats, and Zirc-4 rodlets using magnetron sputter deposition technique. In this process, glow discharge Ar plasma bombards the zirconium-silicide target and the sputtered target atoms condense on the substrate to be formed a thin film. The deposition process was performed under 138 W DC power, 0.53 Pa argon gas pressure, no substrate heating (19 °C), and a rotating sample stage (10 rpm). Detailed procedure and conditions for the deposition is described in the previous work [101]. To achieve thicker coatings and compositional layered coatings, multiple deposition was conducted. A plasma cleaning step (DC 500 W for 5 minutes in 1.6 Pa Ar pressure) was employed between each deposition step to remove surface contamination due to the interruptions in the coating process. For holding the rod samples during the deposition, small aluminum plates were machined to have a single rectangular channel of 3.2 mm in width as shown in Fig. 7.1a. The rod samples fixtured on the short plates were placed on the sputter stage in the vacuum chamber. The rodlets were flipped over 180 ° after the first deposition, improving uniformity of the deposition. The coated samples showed a slight thickness variation in circumferential measurements; thickness difference between the maximum and the minimum thickness was approximately 0.4 μm. Fig. 7.1b shows the ZrSi₂ coated Zirc-4 rodlets with 316 stainless tube extension for quenching experiments.

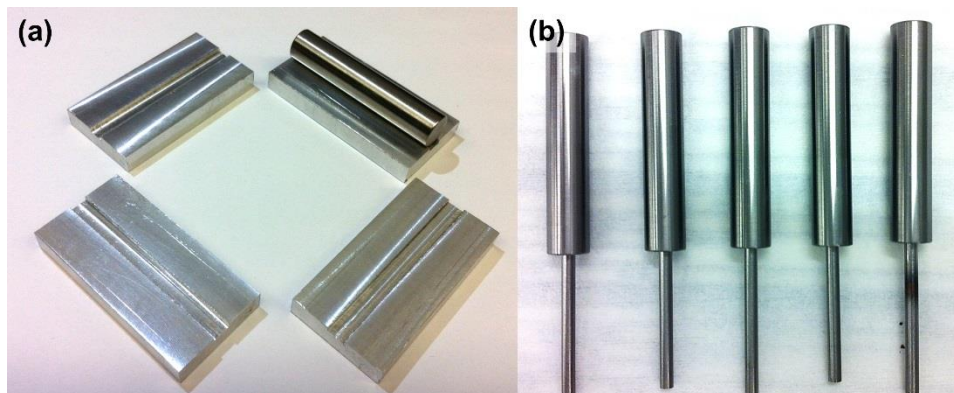


Figure 7.1. Photograph of (a) a cylindrical Zirc-4 sample on the short aluminum plates and (b) ZrSi₂ thin coating on the Zirc-4 samples with the stainless-steel tube extensions.

Quenching experiments for the ZrSi₂ coated Zirc-4 samples, simulating sudden reflood of the overheated fuel rod in an accident scenario, were performed in the deionized water pool under three environmental conditions: atmospheric saturated water, saturated water at 0.5 MPa, and subcooled water (85 °C) at atmospheric pressure. Fig. 7.2 shows the experimental system for the quench test, consisting of the air actuator, the heating zone, and the water pool. The air actuator provides a linear motion to the cylindrical Zirc-4 samples with an approximate velocity of 100 mm/s. In the heating zone, the sample was heated up to 700 °C externally by a 312 W tape heater with fast ramp rate (30 °C /min) and temperature was monitored by a K type thermocouple (1.6 mm in diameter) at the center of the sample. The

measurement uncertainty was assumed to be ± 1.1 °C, as provided by manufacturer (Omega Engineering Corp). The chamber pressure was regulated by compressed argon gas, an inlet pressure regulator, and a back-pressure regulator. The pressure was maintained at 0.5 MPa with a fluctuation of 0.4×10^{-2} MPa during the pressurized experiment. A pressure transducer measured the system pressure with ± 1.0 % uncertainty. The Teflon seal assembly, containing three Teflon O-rings, allowed the linear motion of the sample and maintained the high pressure in the quenching chamber. Temperature of the water pool, filled by 1.4 L of deionized water, was also controlled by an external 624 W tape heater and bubble generation during quenching was visualized through borosilicate windows. A data acquisition system (National Instruments) with a sampling rate of 10Hz was used to record the sample temperature, quenchant temperature, and chamber pressure during quenching experiments.

The first step for the experiment was boiling the deionized water in the quenchant pool for 20 minutes to remove any dissolved gas before controlling system conditions (e.g. increasing pressure or decreasing water temperature). When temperature of the sample reached 700 °C, the air actuator was activated to plunge the sample into the water pool. The transient boiling behavior was analyzed using the temperature history of the sample and the bubble dynamics. Boiling curves (i.e. surface temperature vs. surface heat flux) were estimated by commercial inverse heat transfer software, INTEMP (Version 5.1., Nov. 2009) to determine the transition point in boiling regimes. The conventional uncertainty analysis for the ill-posed problem is difficult but detailed sensitivity analysis for the INTEMP model has been performed in a previous study [102], showing that the outputs appeared to be reliable. Furthermore, a minimal uncertainty of INTEMP calculations for surface temperature and heat flux during water quench experiment of cylindrical Zr samples was reported by Kang et al. [103]. In addition, surface roughness and static water contact angle for the quenched samples were measured by a white light interferometry microscope (Zygo optical profilometer) and water contact angle measurement instrument (Dataphysics OCA 15), respectively.

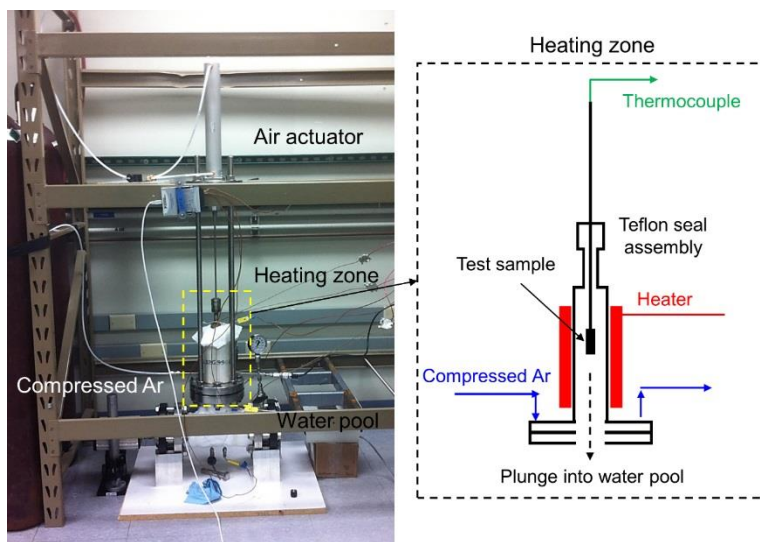


Figure 7.2. Photograph of the quench test facility and schematic illustration of the heating zone.

7.2. Characterization of Coated Surface After Quenching Tests

Quenching experiments of Zirc-4 tubes coated with ZrSi_2 of 2.1 μm in average thickness were performed to examine an effect of the coating on water quenching performance and a robustness of the coating under thermal shock. Results of surface characterization for the bare sample and the ZrSi_2 coated sample after three repeated quench tests are shown in Fig. 7.3. The bare surface reveals minor scratches with directionality from the polishing process, and the coated surface shows the typical sputter coating

morphology with a bulbous structure. Both surfaces were smooth so that average surface roughness (R_a) for the bare surfaces and the coated surfaces were $0.19 \pm 0.01 \mu\text{m}$ and $0.21 \pm 0.01 \mu\text{m}$, respectively. In addition, both surfaces were wettable - the static water droplet contact angle for the bare surfaces and the coatings were $86 \pm 3^\circ$ and $54 \pm 8^\circ$, respectively. Average oxide scale thickness of $3.6 \mu\text{m}$ was identified on the bare Zirc-4 samples after exposure to three sequential quenching treatments (Fig. 7.3c). It was found that the oxide scale was developed while the sample was heated up to 700°C (initial temperature of quenching) and reacted with steam environment prior to plunging into the water pool. On the other hand, the ZrSi_2 coating mitigated the steam corrosion, leading to formation of submicron oxide layer (approximately $0.3 \mu\text{m}$) on the top of the coating without any cracking, delamination, oxidation of the substrate. The absence of oxidation of the substrate is associated with the protective nature of the ZrSi_2 coating at 700°C as observed in the ZrSi_2 coatings in the steam test, and silicon depletion in the coating was not clearly identified in the experiment.

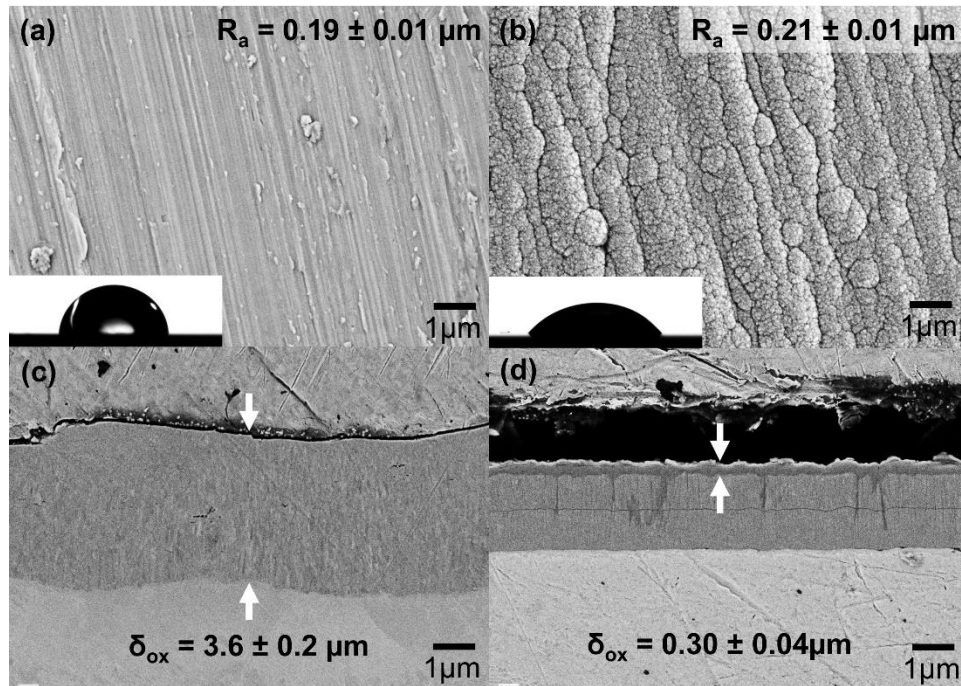


Figure 7.3. SEM surface morphology characterized of (a) bare Zirc-4 surface and (b) ZrSi_2 coated Zirc-4 surface. (Inset) Photograph of a water droplet on each surface condition. Average surface roughness (R_a) for each condition is specified in the images. Cross-sectional SEM image of (c) the bare Zirc-4 and (d) the ZrSi_2 coated Zirc-4, showing thickness of the oxide layer and the coating. All samples were quenched for three times in atmospheric saturated water prior to the characterizations.

7.3. Quenching and Boiling Curves

Quenching performance of the bare Zirc-4 sample and the ZrSi_2 coated sample in atmospheric saturated water was analyzed using the quenching curves (temperature vs. time), the boiling curves (surface heat flux vs. surface superheat), and the high-speed images as shown in Fig. 7.4. The center temperature of the both samples decreases gradually as the cooling progresses. This corresponds to the film boiling regime where vapor film fully covers the hot surface while pulsating in oscillatory motion as shown in the high-speed images right after quenching (0.0s) in Fig. 7.4a. The inflection points for the coating in the quenching curve (Fig. 7.4a) occurred earlier in time during the quench process than the bare sample, which is also confirmed in the high-speed images that the coated sample showed earlier destabilization of vapor film at the bottom of the sample (20.9 s) compared to the bare sample (22.6 s). Furthermore, the boiling curves (Fig. 7.4b)

show that film boiling heat transfer for both surfaces were well matched but the minimum film boiling temperature – closely related to the inflection point in the quenching curve, a lower limit of film boiling regime, for the coating was approximately 20 °C higher than that of the bare surface. From a practical standpoint, it is important for fuel cladding surface to have a higher minimum film boiling temperature during quenching. This is because a heat removal from the heated surface in the film boiling regime is quite limited. The results suggest that the ZrSi₂ surface coating is beneficial to enhance quenching performance to some extent in saturated water at atmospheric pressure.

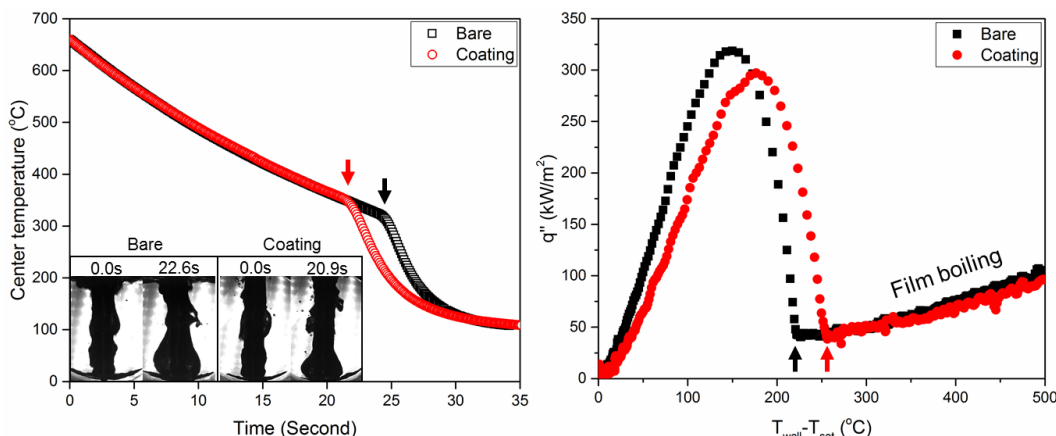


Figure 7.4. (a) Quenching curves, (inset) a snapshot of film dynamics for the bare and coated samples, and (b) boiling curves of the bare sample and the ZrSi₂ coated Zirc-4 samples in atmospheric saturated water. The minimum film boiling points are indicated by the arrows.

Fig. 7.5 summarizes the minimum film boiling temperatures of the ZrSi₂ coated samples at atmospheric saturated water, saturated water (152 °C) at 0.5 MPa, and atmospheric subcooled water (85 °C). The cooling behavior was significantly affected by the environmental conditions and the minimum film boiling point was increased by 6 to 8% with the ZrSi₂ coating regardless of the environmental conditions.

The increase in minimum film boiling temperature by the ZrSi₂ coatings could be explained by thermal properties of the coating. Other surface conditions (i.e. wettability and surface roughness) were similar in both bare surfaces and coated surfaces. It was proposed that thermal properties of wettable surface were dominant factors in controlling quenching heat transfer [102,104]. It was hypothesized that liquid contacts on heated surface can remove a large amount of heat during quenching, leading to a significant temperature drop in localized areas. If a surface has a small thermal conductivity, the localized temperature drop cannot be readily recovered by lateral heat conduction, resulting in the acceleration of collapse of stable film boiling. Therefore, the ZrSi₂ coating is assumed to have a smaller thermal conductivity than Zirc-4.

Previous literature suggests that sputtered coatings have lower thermal conductivities than their bulk counterparts. For example, Cahill and Allen [105] showed that the thermal conductivity of a sputtered SiO₂ film deposited at 100 °C was 77% that of the bulk material even though the film had the same density as the bulk. Also, sputtered TiO₂ film at 250 °C had the thermal conductivity approximately 66% that of the bulk material, but the conductivity of a film deposited at higher temperature (400 °C) approached bulk crystalline TiO₂ [106]. The study suggested that the thermal conductivity of sputtered coating is related to film density, grain size, and concentration of atomic-scale defects (interstitials or vacancies), which were strongly dependent on the temperature of sputter deposition process. Since the ZrSi₂ coating was deposited at the low temperature (19 °C), it is plausible that thermal conductivity of the coating is much less than the reported value for bulk ZrSi₂ ($k = 15.6 \text{ W/m}\cdot\text{K}$ [107]). Furthermore, the ZrSi₂ coating was deposited by the multiple steps to achieve the desired thickness which may cause significant thermal resistance between each

thin layer. Overall, the lower thermal conductivity of the ZrSi_2 coating was attributable to the higher minimum film boiling temperature correlating with an enhanced cooling ability during accident scenarios.

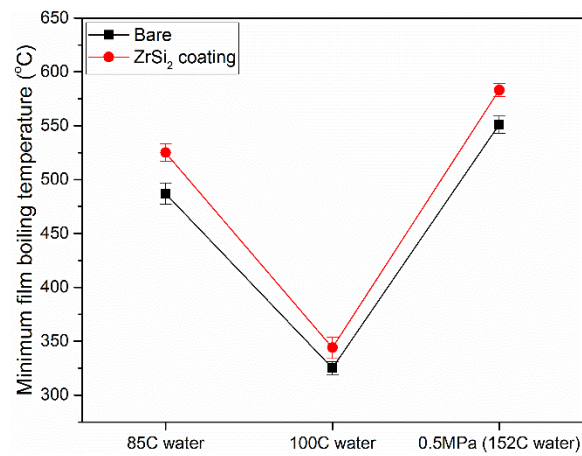


Figure 7.5. Average minimum film boiling temperature for the bare samples and the ZrSi_2 coated Zirc-4 samples in the three experimental conditions – atmospheric subcooled water (85 °C water), atmospheric saturated water (100 °C water), and saturated water at 0.5 MPa (152 °C water). The test was performed at least three times in each condition to ensure statistically significant results.

Publications

1. Journal Publication

1. H.Yeom, B.Maier, R.Mariani, D.Bai, K.Sridharan, Evolution of Multi-Layered Scale Structures during High Temperature Oxidation of ZrSi₂, *Journal of Materials Research*, Vol. 31, n. 21, pp. 3409-3419, 2016
2. H.Yeom, B.Maier, R.Mariani, D.Bai, S.Fronek, Peng Xu, K.Sridharan, Magnetron Sputter Deposition of Zirconium-Silicide Coating for Mitigating High Temperature Oxidation of Zirconium-Alloy, *Surface and Coatings Technology*, Vol. 316, pp. 30-38, 2017
3. H.Yeom, C.Lockhart, R.Mariani, X.Bai, M.Corradini, K.Sridharan, Evaluation of Steam Corrosion and Water Quenching Behaviors of Zirconium-Silicide Coated LWR Fuel Claddings, *Journal of Nuclear Materials*, Vol. 499, pp. 256-267, 2018
4. H.Yeom, H.Jo, G.Johnson, K.Sridharan, M.Corradini, Transient Pool Boiling Heat Transfer of Oxidized and Roughened Surfaces of Zircaloy-4 during Water Quenching, *International Journal of Heat and Mass Transfer*, Vol. 120, pp. 435-446, 2018
5. H.Yeom, L.He, R.Mariani, K.Sridharan, Ion-irradiation response of complex oxide microstructure of zirconium-silicide, *Applied Surface Science*, in preparation, 2018
6. C.Lockhart, H.Yeom, R.Mariani, K.Sridharan, Polymer derived zirconium-silicide ceramic matrix composite coatings for reactor structural materials, in preparation, 2018

2. Conference Proceedings

1. H. Yeom, B. Maier, R. Mariani, D. Bai, P. Xu, and K. Sridharan, "Development of Zirconium-Silicide Coatings for Accident Tolerant Zirconium-Alloy Fuel Cladding", *Proc. International Congress on Advances in Nuclear Power Plants, San Francisco, CA*, 2016
2. H. Yeom, B. Maier, S. Fronek, G. Johnson, E. Strand, R. Mairani, X. Bai, P. Xu, E. Lahoda, K. Sridharan, Development of Zirconium-Silicide Coatings for Improved Performance Zirconium-Alloy Fuel Cladding, *Proc. 2016 ANS Winter Meeting and Nuclear Technology Expo, Las Vegas, NV*, 2016
3. H. Yeom, H. Jo, B. Maier, M. Corradini, K. Sridharan, G.C. Lee, H.W. Lee, T.K. Kim, M.H. Kim, H.S. Park, "Multi-Functional Zirconium-Silicide Coatings on Zirconium-alloy for Improved Accident Tolerance", *ANS Annual Meeting, San Francisco, CA*, 2017
4. M. Kim, J.Y. Kang, J.M. Kim, H. Noh, G.C. Lee, H.J. Kwak, T.K. Kim, H. Yeom, H. Jo, M. Corradini, K. Sridharan, H.S. Park, "Evaluation of accident tolerant cladding thermally enhanced by anodic oxidation and electrophoretic deposition", *2017 Water Reactor Fuel Performance Meeting, Jeju Island, Republic of Korea*, 2017

3. Conference Presentation/Abstracts

1. International Congress on Advanced Nuclear Power Plants (ICAPP) 2016: Development of Zirconium-Silicide Coatings for Accident Tolerant Zirconium-Alloy Fuel Cladding, San Francisco, CA, April 20th, 2016
2. 4th Annual Collaboration for Advanced Research for Accident Tolerance (CARAT) Cladding Meeting 2016: Development of Zirconium-silicide Coatings on Zr-alloy Cladding for Enhanced Accident Tolerance, Boise State University, Boise, ID, September 9th, 2016
3. Materials Science & Technology (MS&T) 2016: Development of Zirconium-silicide Coating for Enhancement of Accident Tolerance of Zirconium-alloy LWR Cladding Material, Salt Lake City, UT, October 24th, 2016
4. American Nuclear Society Winter Meeting & Expo 2016: Development of Zirconium-Silicide

Coatings for Improved Performance Zirconium-Alloy Fuel Cladding, Las Vegas, NV, November 9th, 2016

5. American Nuclear Society Annual Meeting 2017: Multi-functional zirconium-silicide coatings on zirconium-alloy for improved accident tolerance, San Francisco, CA, June 13th, 2017
6. TMS 2018 Annual Meeting & Exhibition: Enhanced Accident Tolerant Zirconium-silicide Coated LWR Fuel Cladding, Phoenix, AZ, March 11th, 2018

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Appendix: Journal Publications and Conference Proceedings

Evolution of multilayered scale structures during high temperature oxidation of ZrSi_2

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The oxidation behavior of bulk ZrSi_2 at 700, 1000, and 1200 °C in ambient air has been investigated. Parabolic to cubic oxide layer growth kinetics was confirmed by weight gain measurements and the average oxide layer thickness was 470 nm, 6.7 μm , and 37 μm at 700 °C, 1000 °C, and 1200 °C, respectively, after 5 h oxidation tests. Evolution of compositionally modulated nano/micro structures was confirmed in the oxide layer. At 700 °C, Si diffusion resulted in discontinuous Si-rich oxide phases in amorphous Zr–Si–O matrix. At 1000 °C, complex multilayered structures such as fine and coarse irregular spinodal structures, wavy Si-rich oxide, and Si-rich islands evolved. At 1200 °C, additional nucleation of nanoscale ZrO_2 particulate phase was observed. The spinodal structures were confirmed to be crystalline ZrO_2 and amorphous SiO_2 , and the thermodynamic driving force for phase evolution has been explained by extension of liquid miscibility gap in the binary ZrO_2 – SiO_2 phase diagram.

I. INTRODUCTION

In light water reactors (LWR), zirconium-alloy (Zr-alloy) fuel claddings have been widely used for over four decades due to the excellent neutron transparency of Zr, and combination of corrosion resistance and mechanical properties in normal operating conditions.¹ However, in high temperature environments (1000 °C or higher) as may be the case during accident scenarios, significant degradation of the Zr-alloy cladding occurs. Profuse exothermic oxidation occurs (with associated hydrogen production) leading to a loss in mechanical integrity of the cladding. Furthermore, zirconium-oxide undergoes phase transformations as the temperature rises, which promotes its spallation and exacerbates cladding degradation.^{2–5} Efforts to address this challenge have been aimed at replacing Zr-alloy as cladding material with other materials such as FeCrAl alloys and SiC–SiC composites.^{2,6–9} Another approach involves deposition of oxidation-resistant coatings on Zr-alloy cladding. In this regard, chromium,^{10,11} Ti_2AlC ,¹² and TiN¹³ coatings have been investigated.

It is well known that transition metal-silicides have outstanding oxidation resistance and structural properties at high temperatures. For example, MoSi_2 has been extensively

studied on account of its outstanding oxidation resistance.¹⁴

However, this material has been reported to suffer from accelerated pest oxidation at low temperatures resulting in a porous and nonprotective oxide scale.^{15,16} ZrSi_2 has been studied to a much lesser extent, but appears to be a more appropriate candidate for a coating for the nuclear fuel cladding application from the standpoints of neutronics and greater compatibility with the underlying Zr-alloy substrate due to its oxophilic nature which is expected to result in better bonding to the native oxide film on the Zr-alloy. Moreover, ZrSi_2 has high Young's modulus (~ 200 GPa) and high compressive yield strength at high temperatures (~ 200 MPa at 1000 °C).¹⁷ However, there have been only limited studies on the evaluation of oxidation behavior of ZrSi_2 at high temperatures. It has been reported that oxidation of ZrSi_2 in dry oxygen and steam does not result in a continuous SiO_2 layer, differing in this regard from other silicides (CoSi_2 , CrSi_2 , NiSi_2 , PtSi_2 , and TiSi_2) regardless of oxidation temperature.¹⁸ The long term isothermal oxidation (600–1100 °C for 160 h) of aluminum alloyed (4 at.% addition) ZrSi_2 showed high oxidation resistance with two oxidation stages above 700 °C: early stage (formation of ZrSiO_4 , ZrO_2) and steady-state stage (formation of Al_2O_3).^{19,20} Thermogravimetry and differential thermal analysis experiments of ZrSi_2 powders up to 1450 °C suggest complex step reactions with combination of ZrO_2 , SiO_2 , and ZrSiO_4 formation.²¹ Nevertheless, the oxidation data of bulk ZrSi_2 at high temperature are still limited.

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In this study, the oxidation behavior of dense bulk forms of ZrSi_2 in high temperature air (700, 1000, and 1200 °C) has been explored. A temperature of 700 °C was chosen to determine whether material degradation at low temperature occurs like MoSi_2 while higher temperatures (1000 and 1200 °C) simulate a postulated loss of coolant accident scenario in LWR.²² In addition, Zircaloy-4 (Zry-4) was also oxidized under similar conditions as a base-line for comparison with ZrSi_2 . All oxidized samples were rigorously characterized with the goal of understanding compositional and morphological evolution of microoxide and nanooxide structures.

II. EXPERIMENTAL

A. Materials

Commercially available dense ZrSi_2 (American Elements Inc., Los Angeles, CA) with a reported purity of >99.5% and Zircaloy-4 plate (ATI Wah Chang, Albany, OR, referred to as Zr-4 henceforth) were procured for this study. The density of the dense ZrSi_2 was about 95% of theoretical densities,²³ respectively. The phases in the as-received materials were confirmed by x-ray diffraction analysis (XRD), but few micron-sized Si particles were revealed in as-received ZrSi_2 matrix as an impurity. All ZrSi_2 samples were cut and ground into approximately $12.7 \times 12.7 \text{ mm}^2$, 6.4 mm thick square coupons, and Zr-4 coupons were 3.2 mm thick.

B. Air oxidation tests

All six faces on the samples were ground progressively with 320, 600, 800, and 1200 grit SiC papers and then ultrasonically cleaned with methanol and acetone. The dense ZrSi_2 and the Zry-4 samples were exposed at 700, 1000, and 1200 °C in stagnant ambient air. The samples were removed each hour for weight change measurements (as an initial measure of the extent of oxidation) performed with Satorius microprecision balance (model#CPA26P) with 0.002 mg resolution. The fast cooling with ambient air was conducted because slow cooling may not be able to preserve microstructures that evolved at high temperatures and to minimize this possibility of any changes during cooling.

C. Characterization

Surface morphology and evolution of oxide structures in cross-section were characterized by Zeiss LEO Scanning Electron Microscope (SEM; Carl Zeiss AG, Oberkochen, Germany) integrated with Energy Dispersive Analysis System (EDS). XRD (Bruker Corporation, Billerica, Massachusetts) with Cu K_α radiation was performed to identify oxide product phases and the very near-surface composition was evaluated by Thermo-Scientific $\text{K}\alpha$ x-ray Photoemission Spectroscopy (XPS; Thermo Fisher

Scientific, Waltham, Massachusetts). To identify oxidized structures at high magnification and resolutions, thin foils of the sample surface were lifted out by a Zeiss Auriga Focus Ion Beam (FIB; Carl Zeiss AG) milling and imaged with a Tecnai 12 Transmission Electron Microscope (TEM; FEI Company, Hillsboro, Oregon) and Titan Scanning TEM in conjunction with EDS (STEM-EDS; FEI Company).

III. EXPERIMENTAL RESULTS

A. Oxidation kinetics and oxidation products

The kinetics of oxidation of the dense ZrSi_2 was determined by weight change measurements at each hour during oxidation. The weight gain values (per unit area of the sample) of Zry-4 and dense ZrSi_2 are shown in Fig. 1. As may be noted, the weight gain of the dense ZrSi_2 is negligible compared to that of the Zry-4 at the high temperatures. The Zry-4 showed the formation of a thick oxide scale and its spallation led to weight reduction at 1000 °C (4 h) and 1200 °C (3 h) as shown in Fig. 1(a). On the other hand, the dense ZrSi_2 appeared to be stable without significant degradation at the high temperatures.

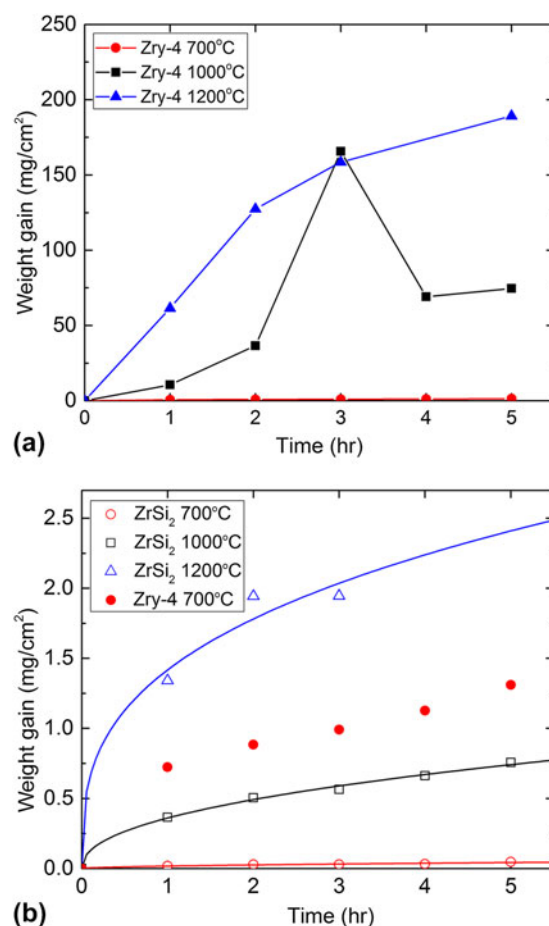


FIG. 1. Weight gain versus time for (a) Zry-4 and (b) dense ZrSi_2 samples constructed with least square fits at 700, 1000, and 1200 °C in air.

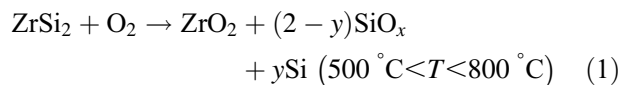
It is worth noting that no pest oxidation was observed on the surface of the ZrSi₂ samples. Minor chipping on the edge of the dense ZrSi₂ samples was observed at 1200 °C after 3 h oxidation. Therefore, the weight gain values at 5 h have not been reported in Fig. 2(b). The general oxidation kinetics follows a power law. The oxidation kinetics at 700 and 1000 °C follow approximately a parabolic rate law while at 1200 °C follows more closely the cubic growth rate law. More protective nature with increasing temperatures has been reported in MoSi₂ and TiSi₂ as well, resulting from denser SiO₂ formation.^{15,24,25} The weight gain relationships are empirical and were plotted with the limited data points so that it is difficult to elucidate physical and chemical processes of the oxide growth. Nevertheless, the weight gain trends imply that the ZrSi₂ oxidation process is controlled by the diffusion of charged species (e.g., Si⁴⁺, O²⁻) through the oxide dictating the oxide growth rate.²⁶

The oxide layer thickness was measured in SEM cross-sectional images and shown in Fig. 2. The average oxide layer thickness of the dense ZrSi₂ at 700 °C, 1000 °C, and 1200 °C for 5 h oxidation was determined to 470 nm, 6.7 µm, and 37 µm, respectively. In addition, the oxide layer thickness at 1000 °C for 15 h oxidation was 12 µm, which considered together with other exposure times at this temperature is indicative of parabolic oxidation kinetics at 1000 °C. Furthermore, no spallation and delamination of the oxide layer were observed and only minor cracks were identified in unreacted ZrSi₂ matrix underneath the oxide scale at 1200 °C possibly due to thermal cycling due to periodic removal of samples from the furnace.

Although thickness of the ZrSi₂ oxide layer formed at high temperatures is significantly lower than that formed on Zr-4, the oxide scale is much thicker than for TaSi₂, MoSi₂, and WSi₂ in the similar oxidation tests (1000 °C air) reported in literature.^{27,28} One of possible reason for this is the thermodynamically favored ZrO₂ formation in ZrSi₂ oxidation. Fig. 3 shows Gibbs free energy formation of oxide per a mole of O₂ of Si as well as Ta, Ti, Mo, W, and Zr, which was calculated by HSC Chemistry thermodynamics software. In these other metal-silicides except for Ti, selective oxidation of Si leads to the formation of a continuous oxidation resistant SiO₂ layer²⁹ while the absence of continuous SiO₂ layer in ZrSi₂ may result in

relatively faster oxide growth. Likewise, TiSi₂ has at least five times higher oxidation rate compared to MoSi₂.²⁰

The phases present in the oxide layer formed at different temperatures for 5 h exposure were identified by full-theta XRD analysis and the results are shown in Fig. 4. At 700 °C oxidation [Fig. 4(a)], pronounced diffracted peaks stemming from unreacted ZrSi₂ and weak Si and monoclinic ZrO₂ (m-ZrO₂) peaks were identified. At 1000 °C [Figs. 4(b)] and 1200 °C [Fig. 4(c)] oxidation, intensity of m-ZrO₂ was remarkably increased and weak Si peaks were also seen. Grazing incidence XRD scan (2° incident beam angle) showed the same results. For higher temperatures, the intensity of the strongest m-ZrO₂ peak at 28° (−111) gets sharper but the ZrSi₂ strongest peak at 39° (131) gets weaker and broader, which corresponds to thicker ZrO₂ oxide layer at higher temperature. In addition, absence of peaks of thermodynamically favored SiO₂ and zircon (ZrSiO₄) phases observed in Zr–Si–O system does not preclude their presence, since they may be present as amorphous phases. During the selective oxidation of Zr in ZrSi₂, some Si may be newly formed as an intermediate product which represents the weak silicon peak at 47° (220). Geßwein et al.²¹ postulated selective oxidation producing SiO₂ and Si at low temperature [as shown in Eq. (1)] from thermogravimetric experiments of ZrSi₂ powders oxidation in air.



Additionally, it is not surprising that tetragonal-zirconia phase which is stable above 1000 °C based on Zr–O binary phase diagram³⁰ is not observed in Fig. 4. This is because our XRD analysis was conducted at room temperature so that most tetragonal zirconia transformed to monoclinic zirconia during cooling.²²

B. Microstructural evolution oxide layer in the oxidized ZrSi₂

Given that both Zr and Si have very negative Gibbs free energy of oxide formation of each oxide and possible selective and nonselective oxidations of Zr in ZrSi₂ creates the potential to produce complex multilayered

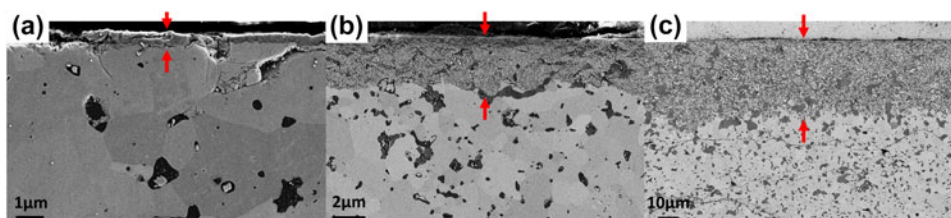


FIG. 2. Cross-sectional SEM images of the dense ZrSi₂ at (a) 700 °C, (b) 1000 °C, and (c) 1200 °C for 5 h exposure in air. The red arrows indicate the oxide layer between a mounting resin and unreacted ZrSi₂.

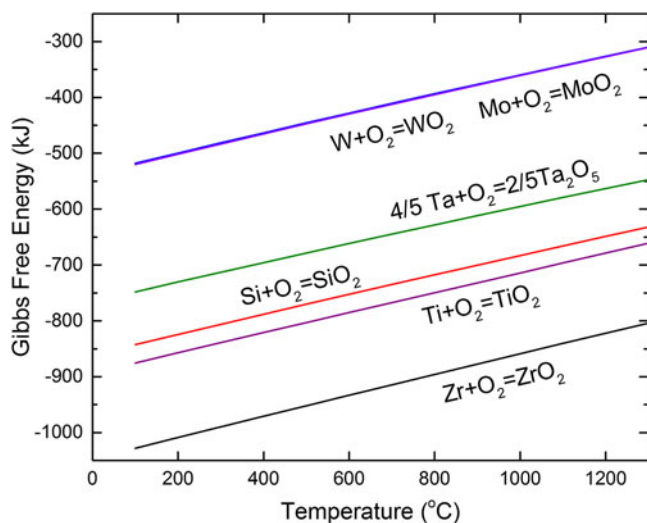


FIG. 3. Gibbs free energies of oxide formation for Zr, Ti, Si, Ta, W, and Mo per 1 mole O₂, calculated by HSC Chemistry thermodynamics software.

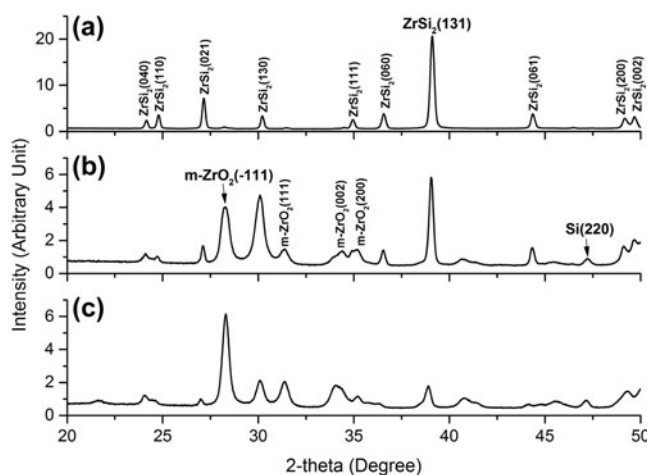


FIG. 4. XRD patterns of the ZrSi₂ oxidized at (a) 700 °C, (b) 1000 °C, and (c) 1200 °C for 5 h showing monoclinic zirconia, silicon, and unreacted ZrSi₂ peaks.

structure, which may be beneficial for protection of Zr-alloy fuel cladding under accident conditions.

1. Surface morphology evolution

To investigate the compositional and morphological evolution of the oxide layer at high temperatures, plan-view SEM-EDS examinations were first performed for samples exposed to each of the temperatures for 5 h. Figure 5(a) shows SEM image of the surface of the as-received ZrSi₂ and Fig. 5(b) shows surface of ZrSi₂ sample that was subject to oxidation at 700 °C for 5 h. Figures 5(c) and 5(d) show results of EDS analysis of the oxide layer. Micron-sized spherical phases were observed to evolve on the oxidized surface [Fig. 5(b)].

Semiquantitative EDS point scan confirmed that there were local variations in the concentration of Si, Zr, and O on the surface and the spherical phases were enriched in Si [i.e., point 1 and 2 in Fig. 5(c)]. This represents a significantly higher Si concentration than in the as-received ZrSi₂ for which the Zr-to-Si ratio was 1:2.4 as determined by our XPS, to be discussed later. Therefore, the micron-scale spherical phases appear to be Si-rich oxides formed by Si diffusion from the surrounding area.

On surfaces oxidized at higher temperatures, the surface morphology was different as shown in Fig. 6 for samples oxidized at 1000 and 1200 °C. The Si-rich humps were not clearly identified but nanoscale precipitation of oxide phase particulates (40–100 nm in size) appeared, particularly, on the surface of samples oxidized at 1200 °C [Fig. 6(b)]. The imaging contrast between the background matrix and oxide particulates suggests differences in their compositions and TEM-EDS analysis determined that these nanosized particulates were ZrO₂ as will be discussed later. At 1000 °C, the fine oxide particles also emerged on the surface but the size of structure was too small to be quantified in the SEM image.

To understand the structural evolution at the surface during high temperature, XPS analysis was performed. The chemical states of Si, Zr, and O were acquired over a 400 μm diameter circular region on the surface of samples oxidized at each of the temperatures for 5 h and the results are shown in Fig. 7. The intensity of Si 2*p* binding energy peak increases with increasing oxidation temperature—the peak binding energy shifted +1 eV (102.8 eV → 103.8 eV) between samples oxidized at 700 °C and those oxidized at higher temperatures (1000 and 1200 °C). On the other hand, signal intensity of the Zr 3*d*_{3/2} and Zr 3*d*_{5/2} binding energies decreased with increasing oxidation temperature. Here, the peak values shifted −0.7 eV at 1000 °C compared to 700 °C (183.6 eV → 182.9 eV). The O 1*s* binding energy associated with the elements showed the same trends with respect to temperature. The intensity of O 1*s* binding energy associated with Zr atom decreased but that of Si atom increased with the binding energy shifts, indicating fundamental differences compositional shifts between 700 °C and 1000 °C/1200 °C exposures. Based on the reported XPS binding energies,³¹ the binding energy of Si 2*p* and Zr 3*d* at 1000 and 1200 °C corresponded to SiO₂ and ZrO₂ but those in 700 °C did not clearly match with the simple oxides. The shifts in x-ray photoelectron peaks are likely associated with a transition in binding states. Such shifts have been reported in a complex mixed oxide (i.e., ZrSiO₄) in comparison to simple oxides (i.e., ZrO₂ and SiO₂) due to different covalency of cations. The Si 2*p* bonding is more covalent but the Zr 3*d* is more ionic in ZrSiO₄.^{32,33} Therefore, it is speculated that at 700 °C an amorphous Zr–Si–O phase forms, however, at

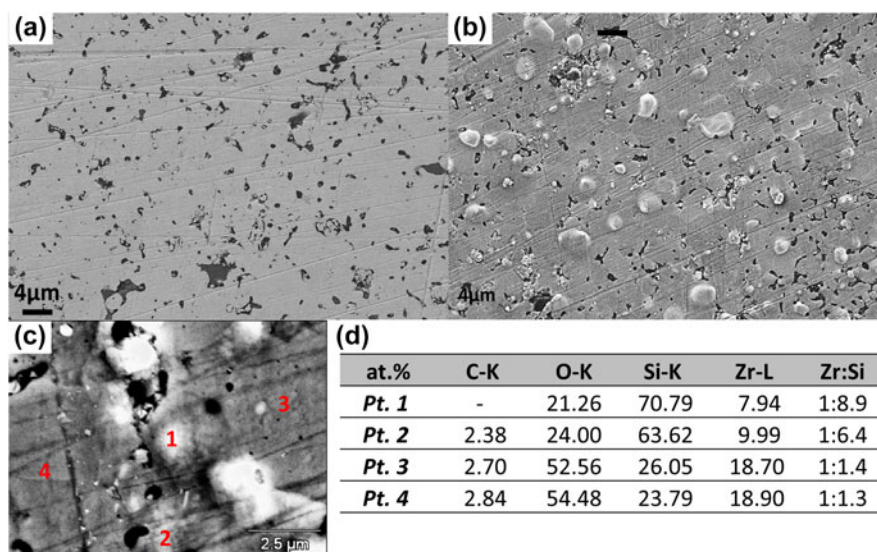


FIG. 5. Plan-view of SEM images of (a) as-received ZrSi_2 , (b) ZrSi_2 oxidized at 700 °C for 5 h, (c) high voltage SEM (12 kV) image of the oxidized sample, and (d) EDS compositions in regions indicated in (c). Points 1 and 2 indicate the regions of spherical phases shown in the image (b).

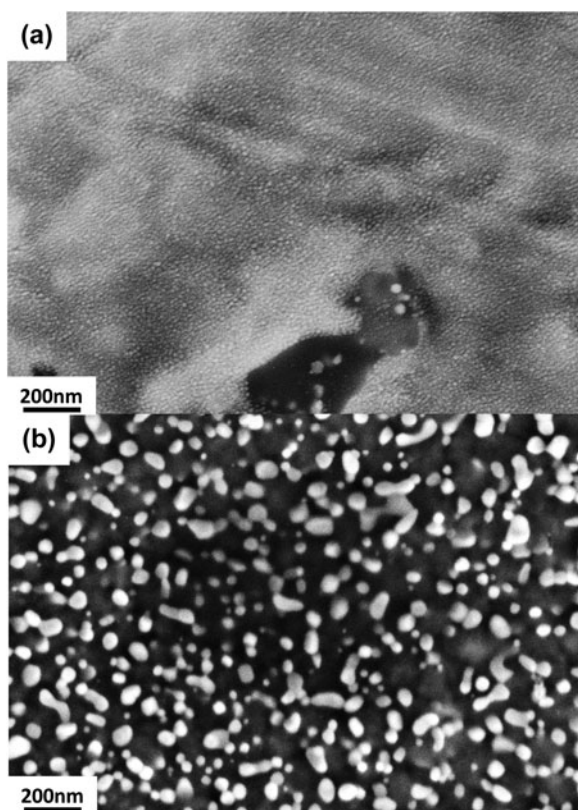


FIG. 6. Plan-view of high magnification SEM images of ZrSi_2 oxidized at (a) 1000 °C for 15 h and (b) 1200 °C for 5 h.

1000 and 1200 °C this phase is not stable but rather decomposes to distinct SiO_2 and ZrO_2 simple oxide phases. This is also in good agreement with phase conversion from amorphous ZrSiO_4 film to simple oxides

at 900 °C annealing (i.e., $\text{Si-O-Zr} \rightarrow \text{O-Si-O} + \text{O-Zr-O}$) reported in a previous study.^{34,35} Interestingly, oxidation product of TiSi_2 at 600 °C in oxygen is glassy Ti-Si-O phase as well.³⁶ The near-surface chemical composition of oxidized surfaces as determined by the XPS technique is summarized in Table I. The variation of the concentration ratio of Zr to Si indicates that there was not only lateral diffusion of species shown in Figs. 5 and 6 but also depth-wise diffusion of species. The compositional ratio of Si to Zr was slightly reduced (less Si) at 700 °C but it increased again (more Si) at 1000 °C and gets doubled at 1200 °C compared to the as-received ZrSi_2 . Based on the published high diffusion rate of Si compared to Zr,^{37,38} it appears that a part of newly formed Si during oxidation diffused inward in the thin oxide layer so that the Si concentration on the surface is diminished during oxidation at 700 °C. However, a net outward flux of Si atoms at the higher temperatures increases the Si concentration on the outer-most surface.

2. Depth-wise structural evolution

To correlate the observed surface chemical and morphological evolution with depth-wise species diffusion, cross-sectional analysis using high magnification STEM imaging was performed (Fig. 8). At 700 °C, 10 h oxidation was carried out to get thicker oxide layer and subsequent STEM analysis showed dark wavy structures [Fig. 8(a)] in the ~ 630 nm thick oxide layer that formed. EDS line scan analysis showed the structures to be Si-rich oxide phase [Fig. 8(b)] and consequently a reduction of Si concentration was identified in the adjacent regions. Based on the STEM observation, the phase identification in XRD, and the binding energy shift in XPS, the major

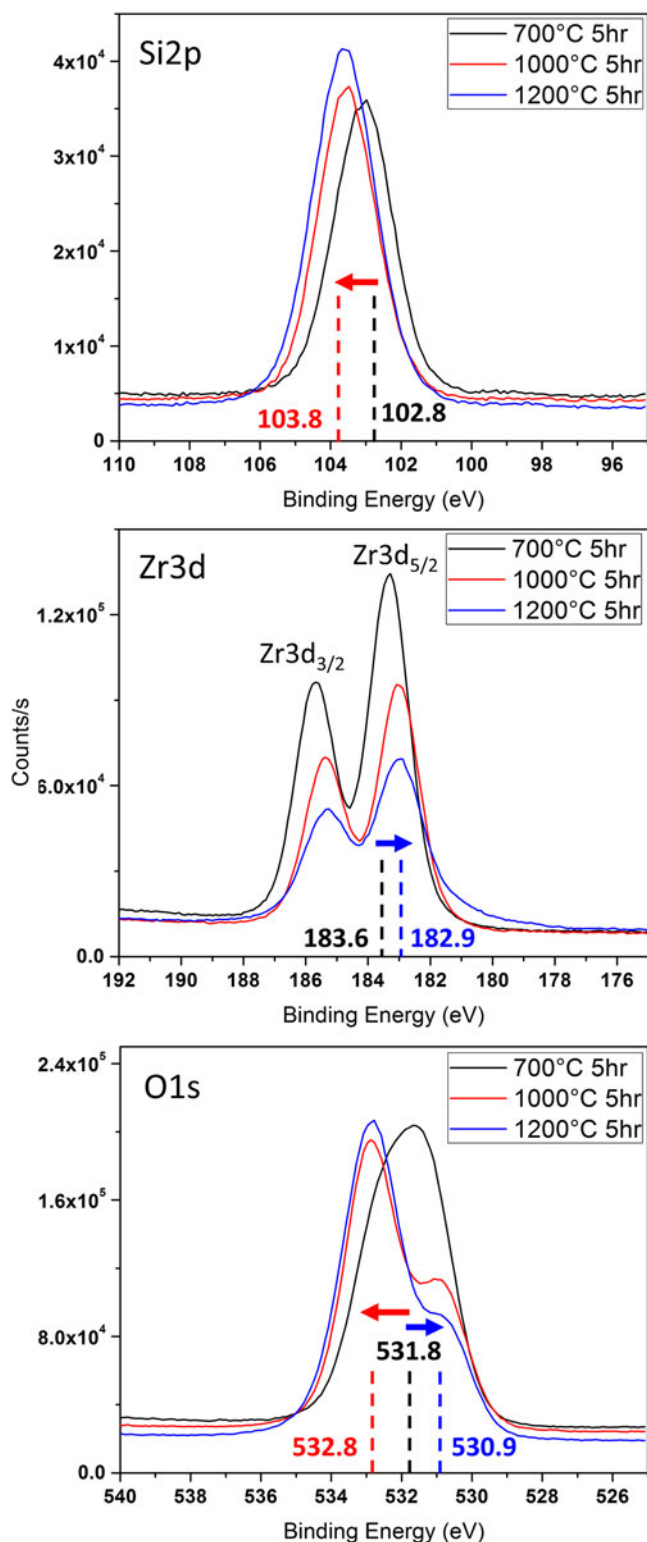


FIG. 7. XPS spectrum (Si 2p, Zr 3d, O 1s binding energy) of ZrSi₂ oxidized at 700, 1000, and 1200 °C after 5 h oxidation. Position of the peak maximum (eV) is specified and the arrows indicate the trend of binding energy shift with increasing temperature (from 700 °C to 1000 °C/1200 °C). The red arrows and blue arrows are associated with silicon and zirconium, respectively.

TABLE I. XPS near-surface chemical compositional analysis of as-received and ZrSi₂ oxidized at high temperatures.

Atomic%	Si 2p	Zr 3d	C 1s	O 1s	Zr:Si
As-polished	32.23	13.59	8.35	45.84	1.0:2.4
700 °C for 5 h	21.16	11.40	1.79	65.64	1.0:1.8
1000 °C for 5 h	23.38	8.60	3.37	64.65	1.0:2.7
1200 °C for 5 h	27.86	6.74	1.69	63.72	1.0:4.1

phases in the oxide layer at 700 °C are likely amorphous Zr–Si–O and Si-rich oxide. The cross-sectional images of samples oxidized at 1000 and 1200 °C showed complex nano/micron structures. Four types of structures were identified in the 7 µm oxide layer formed at 1000 °C [please see Figs. 8(c) and 8(d)]: (i) submicron layer with fine structural features, (ii) underlying wavy dark structures, (iii) a thick region consisting of irregular structures, and (iv) unreacted ZrSi₂ region. It is speculated that the wavy structures developed by the inward diffusion of Si at the early stages of oxidation and the nondirectional irregular structures were formed by spinodal decomposition in the amorphous Zr–Si–O matrix, which will be discussed in detail.

Similar evolution of the oxide structures was observed for samples oxidized at 1200 °C for 5 h. A large numbers of Si islands indicated by the red arrow in Fig. 9(a) were identified at the interface between the oxide layer and unreacted ZrSi₂. In addition, charging effects were observed in Fig. 9(a), indicating a fully oxidized structure (bright regions) which has dielectric properties. However, some regions appeared not to be oxidized significantly and manifested as dark and gray areas shown in Fig. 9(b). The nanoscale spherical particulates, which was seen on the plan view image [Fig. 6(b)], were dispersed only in region adjacent to air interface [Fig. 9(c)]. The uniform irregular nanoscale structures are again observed in Fig. 9(d). The EDS analysis [Fig. 10(a)] showed that the less oxidized regions were composed of Si-rich oxide and unreacted ZrSi₂. The origin of the Si-rich oxide is the slow reaction kinetics of SiO₂ growth²⁷ during oxidation of the newly formed Si and some ZrSi₂ were not completely consumed while the oxide layer was developing. The irregular structures seem to consist of ZrO₂ and SiO₂ based on the EDS point scan [point 1 in Fig. 10(b)], corresponding to the Si-depleted regions in the EDS mapping. In addition, the existence of Si islands in the interface between the oxide scale and ZrSi₂ suggests that the selective oxidation occurs at temperatures higher than those reported in temperature (<800 °C).²¹ Due to relatively large SEM-EDS spot size (~1 µm), TEM-EDS analysis was performed to understand mechanism of evolution of this compositionally alternating oxide structure.

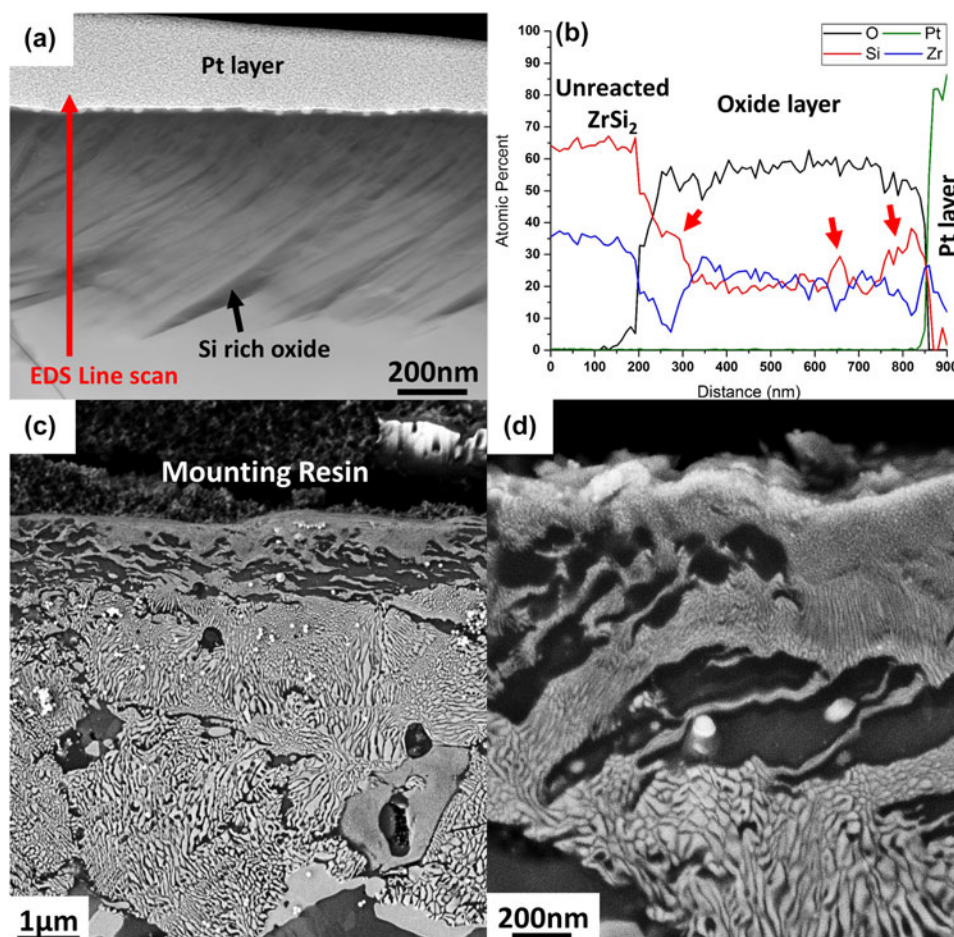


FIG. 8. (a) HAADF STEM cross-sectional image of ZrSi_2 oxidized at 700 °C for 10 h and (b) corresponding EDS line-scan showing composition fluctuation even in the thin (~ 630 nm) oxide layer. The red arrows indicate Si-rich oxide. (c) Cross-sectional SEM image with low voltage (3 kV) of the oxide layer on ZrSi_2 formed at 1000 °C for 5 h at low magnification and (d) and high magnification near the top layer.

The irregular nanoscale structures and spherical phases observed in Figs. 9(c) and 9(d) were analyzed using STEM-EDS (Fig. 11). The high angle annular dark field (HAADF) STEM images of the ZrSi_2 oxidized at 1200 °C for 5 h revealed nanoscale particulate phases [Fig. 11(a)] adjacent to the air interface and the irregular structures [Fig. 11(b)] uniformly dispersed in the entire oxide scale. Since brightness in HAADF images is proportional to atomic number of material, it is speculated that the structures were composed of higher atomic number elements compared to the background matrix material. STEM-EDS analysis confirmed the chemical composition of the structures as shown in Fig. 11(c). The spherical particulates and irregular structures were crystalline ZrO_2 in SiO_2 background matrix. The fuzzy ring diffraction pattern [inset, Fig. 11(b)] of the background matrix suggests that the SiO_2 phase is amorphous, in agreement with the XRD result where no crystalline SiO_2 peaks were identified.

IV. DISCUSSION

A. Spinodal decomposition

As mentioned earlier, a plausible explanation to the formation of an alternating nanolayered structure of ZrO_2 and SiO_2 is phase separation of amorphous Zr-Si-O by spinodal decomposition, a diffusion driven process that occurs in unstable undercooled or supersaturated phases, resulting in homogenous two-phase fine scale mixture.³⁹ Lucovsky et al.^{34,35} first reported that annealing of ~ 400 nm amorphous ZrSiO_4 thin film at 900 °C for 60 s led to chemical phase separation consisting of crystalline ZrO_2 and amorphous SiO_2 based on infrared absorption spectroscopy. A thermodynamic driving force exists if the solid mixture is within unstable spinodal boundary. Kim et al.⁴⁰ estimated the excess Gibbs free energy of mixing in supercooled liquid of ZrO_2 and SiO_2 using a subregular model utilizing the invariant points in pseudo-binary ZrO_2 - SiO_2 phase diagram. In addition, Stemmer et al.⁴¹ predicted extension of the liquid

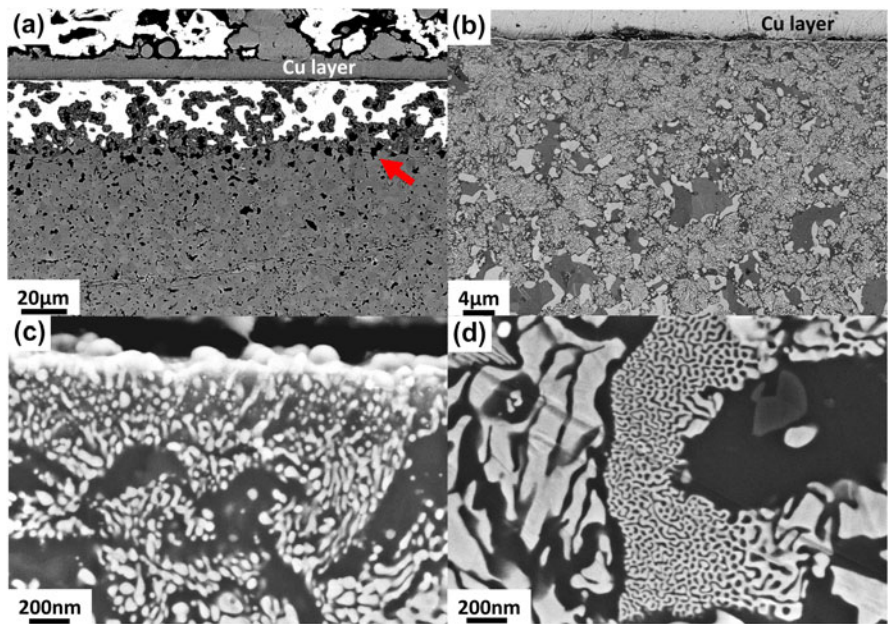


FIG. 9. SEM images of ZrSi₂ oxidized at 1200 °C for 5 h, taken at (a) 12 kV and (b) 3 kV at low magnifications. High magnification 3 kV SEM images (c) at interface between air and oxide layer and (d) at the middle of oxide scale showing different shapes of nanoscale structures.

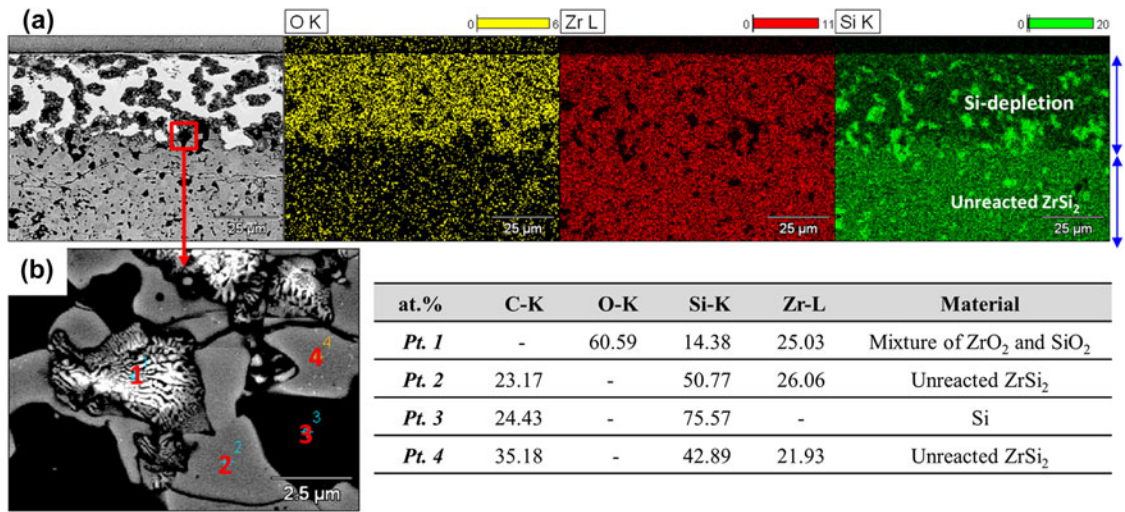


FIG. 10. EDS spectra mapping (a) of the oxidized ZrSi₂ at 1200 °C for 5 h showing Si depleted region, and point EDS analysis (b) at the interface between oxide layer and unreacted ZrSi₂. The carbon signal is an artifact from the mounting resin.

miscibility gap and spinodals to lower temperature using commercially available thermodynamic software and published oxide data. Based on their estimations, the composition of spinodal boundary between 1000 and 1200 °C in ZrO₂ and SiO₂ mixture is in the range of 0.4–0.9 SiO₂ mole fraction and its corresponding decomposed equilibrium phases are ZrO₂ rich phase (0.2–0.4 SiO₂ mole fraction) and SiO₂ rich phase (0.9–0.98 SiO₂ mole fraction). Therefore, it is suggested that there is a thermodynamic driving force that induces spinodal decomposition in ZrSi₂ oxidation at high temperatures.

At 1000 °C, the spinodal structures near the top surface were finer than those at the center of the oxide layer, which may be attributed to ZrO₂/SiO₂ composition effect on Gibbs free energy of mixing. The minimum wave length of phase modulation decreases with increasing negativity of second derivative of Gibbs free energy of mixing.⁴² The absolute value of the negative free energy is maximized at 73% mole fraction of SiO₂ at 1000 °C calculated by the subregular model,⁴¹ which is consistent with Si concentration of the 1000 °C surface, resulting in formation of the finer spinodal structures.

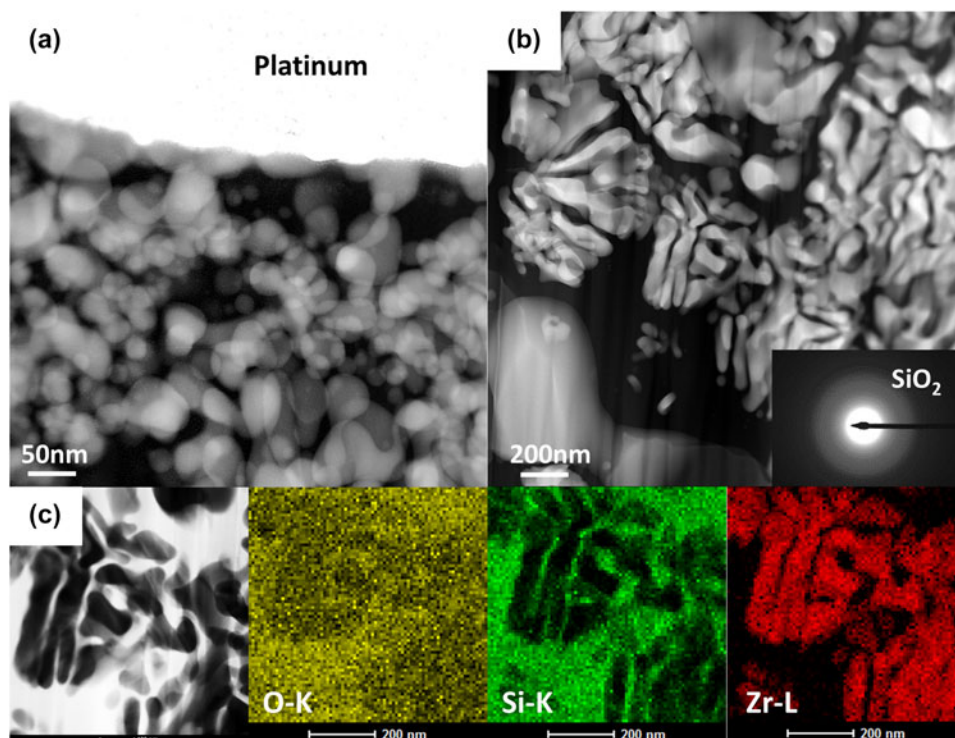


FIG. 11. HAADF STEM cross-sectional images of ZrSi_2 oxidized at 1200 °C for 5 h. (a) nanoscale spherical phases at the interface with air (i.e., top surface) and (b) irregular structures uniformly dispersed in oxide scale. The inset shows SiO_2 diffraction pattern indicating an amorphous structure. The platinum layer was deposited on the top of the sample during sample preparation by FIB. Higher atomic number material has brighter contrast in these images. (c) Bright field STEM image and STEM-EDS elemental mapping images of the irregular structures. These images clearly indicate that the irregular structures consist of ZrO_2 and amorphous SiO_2 .

Additionally, nucleation of the ZrO_2 particulates at 1200 °C on the top surface would also be explained by the extension of the liquid miscibility gap. Due to the highest concentration of SiO_2 on the top surface by outward Si diffusion in oxide layer (see Table I) at 1200 °C, the composition may not be within the spinodal boundary but within miscibility gap. Therefore, nucleation and growth of ZrO_2 in SiO_2 matrix will likely lower its free energy in lieu of spinodal decomposition.

B. Kinetic suppression of crystalline ZrSiO_4 formation

It is worth noting that crystalline ZrSiO_4 was not identified in the ZrSi_2 oxidation even though its formation is preferable in binary ZrO_2 – SiO_2 phase diagram at the temperatures with any composition.⁴³ Most published experiments agree that ZrSiO_4 formation from a reaction of ZrO_2 and SiO_2 requires at least 1300 °C annealing temperature.^{44–47} Formation of crystalline ZrSiO_4 is a solid state reaction, hypothesized that Si^{4+} cations from amorphous SiO_2 diffuses through the highly refractory ZrSiO_4 layer and reacts with t- ZrO_2 to produce new phase and there are no mobile species like in liquid or gas.⁴⁵ Therefore, the growth rate of crystalline ZrSiO_4 is kinetically limited although thermodynamically

favorable. Crystalline ZrSiO_4 formation is expected in ZrSi_2 oxidation at higher temperature (e.g., 1300 °C or 1400 °C) or much longer time oxidation.

C. Summary of ZrSi_2 oxidation

Based on the analysis in this study, a physical model for microstructural evolution during the isothermal oxidation at each test temperature is schematically shown in Fig. 12 in an attempt to develop a picture of microstructural evolution in the oxide layer. At 700 °C, a thin oxide layer consisting of Zr–Si–O amorphous phase matrix with Si-rich oxide wavy structures forms. Additionally, small amount of Si and ZrO_2 was identified in XRD analysis. The role of the newly formed Si by the selective oxidation in the ZrSi_2 oxidation is important. The Si diffuses around the oxide layer and leads to the formation of Si-rich spherical phases on the surface and its inward diffusion induced reduction of Si concentration on the top surface as well as formed Si-rich wavy oxide. Although the composition of the oxide is within the estimated spinodal boundary, mobility of species at this temperature is not enough to show distinct phase separation.

At 1000 °C, in the initial stages of oxidation, the Si diffused inward first when it reacted with oxygen in the thin oxide layer and agglomerated resulting in

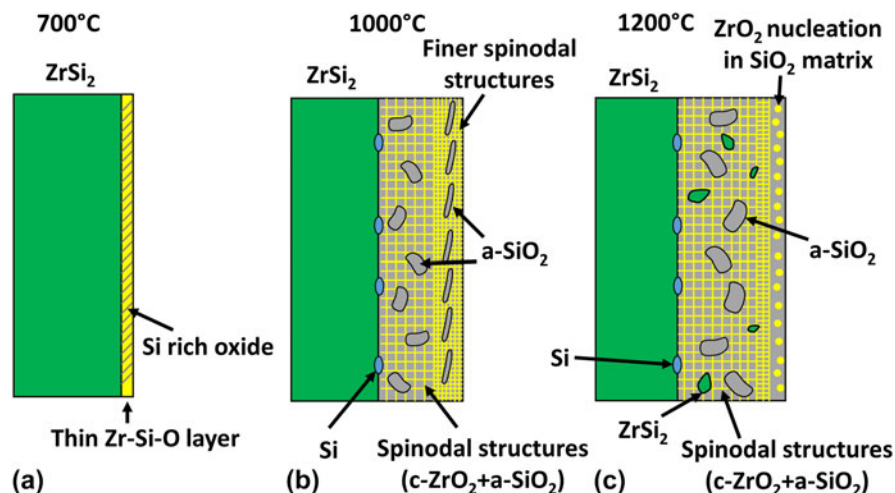


FIG. 12. Schematic illustration of the microstructural evolution during isothermal oxidation of ZrSi_2 at (a) 700 °C, (b) 1000 °C, and (c) 1200 °C. c = crystalline and a = amorphous. The figure is not scaled.

wavy Si-rich oxide structures. The wavy structures seen in 700 °C oxidation tests were likely precursors of those observed at 1000 °C. While oxidation continues, outward diffusion of the newly formed Si dominated as confirmed by the increment of Si concentration at the surface. In the oxide/ ZrSi_2 interface, the amorphous Zr–Si–O mixture decomposed quickly so that the isotropic irregular structures consisting of ZrO_2 and SiO_2 were generated. At the same time, the Si produced Si-rich oxide islands near the spinodal structures.

At 1200 °C, the oxidation behavior was similar to 1000 °C oxidation except for the nucleation of the nanoscale ZrO_2 particulates near the air interface. Due to remarkable outward diffusion of Si ions, the Zr–Si–O mixture was metastable and reduced its free energy by ZrO_2 nucleation. In short, it is suggested that an intermediate unstable Zr–Si–O mixture exists during oxidation of ZrSi_2 at 1000 and 1200 °C, leading to phase separation to ZrO_2 and SiO_2 .

V. CONCLUSIONS

A study to gain and fundamental understanding of the evolution of oxide layer in ZrSi_2 at high temperatures has been performed with the goal of applying ZrSi_2 coatings on Zr-alloy fuel cladding to improve their accident tolerance. ZrSi_2 showed parabolic-cubic oxidation kinetics depending on temperature and its weight gain due to oxidation was negligible compared to Zr-4. Average oxide scale thickness was 470 nm, 6.7 μm , and 37 μm at 700 °C, 1000 °C, and 1200 °C, respectively, for 5 h oxidation. The oxide scale was mechanically stable and there was no evidence of spallation of the oxide layer. At 700 °C, the surface morphology changed in that Si-rich micron-sized spherical phases on the top surface and

Si-rich wavy structures in amorphous Zr–Si–O layer were observed. At 1000 °C, the Si concentration increased at the surface. In the depth-wise direction, fine spinodal structures, wavy Si-rich oxide, coarse spinodal structures, and Si-rich oxide islands were developed. At 1200 °C, similar structures were observed and additionally ZrO_2 particulates in air interface. SEM-EDS and STEM-EDS analysis confirmed spinodal decomposition of Zr–Si–O matrix at 1000 and 1200 °C resulting crystalline ZrO_2 and amorphous SiO_2 and the driving force of their formation was explained by phase instability at 1000 and 1200 °C in ZrO_2 – SiO_2 pseudo-binary phase diagram. Formation of finer spinodal structures at 1000 °C and nucleation of spherical ZrO_2 particulates at 1200 °C may be attributed to high SiO_2 mole fraction by outward Si diffusion. A physical model for oxidation has been proposed wherein Zr–Si–O mixture with newly formed Si undergoes a spinodal phase decomposition into ZrO_2 and SiO_2 , which manifested as a nanoscale assembly of alternating layer of the two oxides. Based on its high oxidation resistance, ZrSi_2 can be considered as a potential candidate coating material for LWR Zr-alloy fuel cladding for improved accident tolerance during a loss of coolant accident. The high temperature oxidation resistance results from the formation of amorphous Zr–Si–O or glassy SiO_2 . However, more tests particularly in steam environment and coating fabrication approaches must be investigated for implementation of this application.

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Magnetron sputter deposition of zirconium-silicide coating for mitigating high temperature oxidation of zirconium-alloy

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ABSTRACT

The air oxidation behavior of zirconium-silicide coatings for three stoichiometries, namely, Zr_2Si , $ZrSi$, and $ZrSi_2$, at 700 °C has been investigated. These three coatings were deposited on a zirconium-alloy substrate using a magnetron sputter process at a low temperature. Argon gas pressure was observed to have a profound effect on the coating microstructure, with lower pressures favoring a denser and more protective microstructure. Coatings of $ZrSi_2$ stoichiometry clearly showed superior oxidation resistance presumably due to the formation of a thin protective oxide layer, consisting of nanocrystalline SiO_2 and $ZrSiO_4$ in amorphous Zr-Si-O matrix. The thermal stability of the coatings was evaluated by annealing in an argon environment, and this also assisted in eliciting the effects of oxidation-induced inward Si migration. Thicker coatings of $ZrSi_2$ were prepared and evaluated for oxidation resistance at 700 °C for longer exposure times, as well as at 1000 °C and 1200 °C. Once again the thin oxide layer provided for significant oxidation resistance. Pre-oxidizing the samples at 700 °C prior to 1000 °C and 1200 °C oxidation tests substantially reduced the extent of oxidation. Insights into the fundamental mechanisms of the oxidation behavior of zirconium-silicide coatings were obtained using a combination of scanning electron microscopy, X-ray diffraction, and X-ray photoelectron spectroscopy techniques. One potential application of these coatings is to enhance the oxidation resistance of zirconium-alloy fuel cladding in light water reactors under normal and accident conditions.

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1. Introduction

Coatings of structural material for elevated temperature applications are becoming increasingly important in a broad spectrum of industries including, aerospace, power generation, and chemical plants. In particular, long term exposure of base materials in high temperature air environment undermines inherent mechanical properties by chemical reaction with ambient oxygen and moisture. For example, the exothermic reaction of zirconium-alloy and high temperature air or steam in high temperature leads to loss of intrinsic mechanical properties due to thick oxide layer formation and hydrogen embrittlement [1–3]. Transition metal silicides, particularly molybdenum-silicide ($MoSi_2$) have been extensively used as coatings for graphite, Molybdenum, and Niobium structural material in the high temperature applications due to its excellent oxidation resistance and mechanical properties [4–6]. However, there is very limited literature on zirconium-silicide in regards to

oxidation or in its use as a coating material. Zirconium silicides (Zr_xSi_y) have high melting points (e.g., $ZrSi$ and Zr_3Si_2 melts at 2203 °C and 2215 °C, respectively [7]). In high temperature air, formation of a passive oxide layer, outstanding oxidation resistance SiO_2 and $ZrSiO_4$, suggest that zirconium-silicide could be good candidate oxidation resistant coating material for high temperature applications [8,9]. In particular, the application of zirconium-silicide coatings on zirconium alloys appears logical given the inherent compatibility between the coating and substrate materials, and no previous studies have been reported on the oxidation behavior of this particular coating-substrate system.

In this study, magnetron sputter deposition of zirconium-silicide on Zircaloy-4 substrate has been explored. To maximize oxidation resistance, deposition parameters and coating compositions have been investigated with characterization of oxidation behavior at 700 °C in air and of thermal stability at 700 °C in argon environment. A temperature of 700 °C was selected to avoid excessive substrate oxidation and to evaluate a formation of non-protective oxide scale like $MoSi_2$ [4,10]. Finally, the optimized zirconium-silicide coating was prepared and oxidized at 1000 °C and 1200 °C in ambient air to evaluate oxidation resistance, which demonstrates potential feasibility of the zirconium-

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silicide coating for zirconium-alloy cladding in light water reactors under potential accident scenarios.

2. Experimental procedure

Test flat coupons of Zircaloy-4 (referred to henceforth as Zirc-4, nominal composition: 0.07 wt% Cr, 0.18 wt% Fe, 0.09 wt% O, and balanced Zr) substrates for deposition of zirconium-silicide coatings were prepared by sectioning square samples $12.7 \times 12.7 \text{ mm}^2$, 2.8 mm thick in dimensions. The samples were then ground successively with 320 grit and 600 grit SiC abrasive paper followed by cleaning with acetone and methanol. Three compositions of zirconium-silicide sputter targets (i.e., Zr_2Si , ZrSi , and ZrSi_2) were procured from a commercial vendor. The sputter targets were 76 mm in diameter and 3.2 mm in thickness. The targets were of 99.5% nominal purity and with 3.2 mm thick copper backing plates for enhancing thermal conductivity during the deposition process.

Prior to initiating the coating deposition process in the magnetron sputter system, the substrates were subjected to in-situ plasma cleaning (dc 500 W for 5 min under 1.6 Pa argon pressure) to remove any residual surface contamination and native oxide layer on the surface of the substrate. Zirconium-silicide coating deposition was performed using a base pressure of 2.6×10^{-4} Pa. Argon sputter gas pressures were 0.53 Pa and 1.33 Pa with a flow rate of 20 sccm – these parameters were selected based on previous studies of magnetron sputter deposited coatings for high-temperature oxidation resistance [11,12]. DC sputter power was 138 W. The distance between the sputter target and the sample stage was 150 mm and the sample stage was rotated at 10 rpm during the deposition to achieve improved uniformity of the coating. The deposition was performed at 19 °C, as monitored in situ by thermocouples, in order to avoid any phase transformations and thermal stresses in the coatings. In order to investigate the effect of argon pressure and composition of coating on oxidation resistance, the depositions were performed under conditions listed in Table 1. The coating deposition for a single step took 150 min, and six steps were performed to achieve thicker coatings that were also investigated in this study. For this multiple step deposition, a plasma cleaning step was employed between the steps to remove any contamination due to interruptions in the coating process. In addition to Zirc-4 substrates, the coatings were also deposited on plasma cleaned Si (100) wafers, which were used for measuring film thickness and observing coating cross-sectional microstructure.

Isothermal oxidation tests were performed at elevated temperatures in a commercial furnace (e.g., Lindberg box furnace, model#51442). Initial studies involved oxidation tests at 700 °C in ambient air for exposure durations of up to 5 h, with samples being removed each hour for weight change measurements (as an initial measure of the extent of oxidation) performed with Satorius micro-precision balance (model#CPA26P) with 0.002 mg resolution. Annealing of the coatings was carried out in argon environment to understand high temperature stability, which then was used to optimize the multi-step thicker coatings. For this, the samples were encapsulated in argon back-filled quartz

tube along with pure zirconium granules to reduce residual oxygen gas during annealing. The thicker coatings produced by multiple tests were tested for oxidation at 700 °C for 20 h, at 1000 °C for 1 h, and 1200 °C for 10 min. Table 1 summarizes the salient features of this experimental study.

Surface morphologies and cross sectional microstructure of the as-deposited, oxidized, and annealed zirconium-silicide coatings were characterized by Zeiss LEO Scanning Electron Microscope (SEM) in conjunction with Energy Dispersive Analysis System (EDS). Phase identification of the coatings was conducted using Bruker D8 Discovery X-ray diffraction (XRD) system with $\text{Cu K}\alpha$ radiation. Diffraction peaks were acquired from 30° to 90° with coupled 2 θ mode and from 30° to 50° in 2 θ with a 2° grazing incident beam. To identify phases in the as-deposited coatings, thin foils of the coatings were prepared by a Zeiss Auriga Focus Ion Beam milling and imaged with a Tecnai 12 Transmission Electron Microscope (TEM). Very near-surface composition and chemical bonding of phases was evaluated by Thermo-Scientific $\text{K}\alpha$ X-ray Photoemission Spectroscopy (XPS). Prior to the binding energy acquisition, surface cleaning was performed by 3 keV Ar ion source for 30 s under high vacuum to remove any residual surface contamination.

3. Results and discussion

3.1. As-deposited thin coatings

Elemental composition of the very near surface of the as-deposited coatings, as analyzed by the XPS, was consistent in trend with the corresponding target chemistry. Argon gas pressure during the process did not influence the coating composition. Grazing incident XRD patterns showed only peaks corresponding to zirconium from the underlying substrate and no peaks corresponding to the coatings was observed for any of the coating stoichiometries (Fig. 1).

Surface morphology and cross sectional microstructure of the coatings, were investigated using SEM. The coatings showed uniform and smooth surface with no indication of spallation. No noticeable differences in surface topography and microstructure were identified in coatings deposited using the different target compositions. On the other hand, argon gas pressure influenced microstructure significantly as shown for example for ZrSi_2 in Fig. 2. The ZrSi_2 #1 coating deposited at higher argon pressure (i.e., 1.33 Pa) exhibited relatively rougher surface and showed nanometer scale gaps in the microstructure (Fig. 2a). Cross-sectional fracture surfaces of these coatings deposited on Si substrate showed tapered columnar microstructures which are revealed more clearly in Fig. 2c. In contrast, the lower argon pressure (i.e., 0.53 Pa), ZrSi_2 #2 coating, exhibited short and dense columnar structures with smoother surface, which are shown in Fig. 2b and d. The observation is in good agreement with Thornton's model [13,14] suggesting that the columnar tapered morphology of the films is a result of atomic shadowing and a low mobility of sputtered atoms on the growing surface at low temperatures. In addition, this morphology would be promoted by increased scattering between argon atoms and target atoms at higher argon pressures. It is expected that the nanoscale gaps

Table 1
Summary of zirconium silicide coatings deposited and investigated in this study.

Sample ID	Target composition	Ar pressure (Pa)	Deposition rate (nm/min)	# of steps	Experimental conditions
Zr_2Si #1	Zr_2Si	1.33	6.12	1	700 °C air for 5 h
ZrSi #1	ZrSi	1.33	5.81	1	700 °C air for 5 h
ZrSi_2 #1	ZrSi_2	1.33	5.39	1	700 °C air for 5 h
Zr_2Si #2	Zr_2Si	0.53	5.30	1	700 °C air for 5 h 700 °C Ar for 5 h
ZrSi #2	ZrSi	0.53	4.97	1	700 °C air for 5 h 700 °C Ar for 5 h
ZrSi_2 #2	ZrSi_2	0.53	4.80	1	700 °C air for 5 h 700 °C Ar for 5 h
ZrSi_2 #3	ZrSi_2	0.53	4.80	6	700 °C air for 20 h 1000 °C air for 1 h 1200 °C air for 10 min

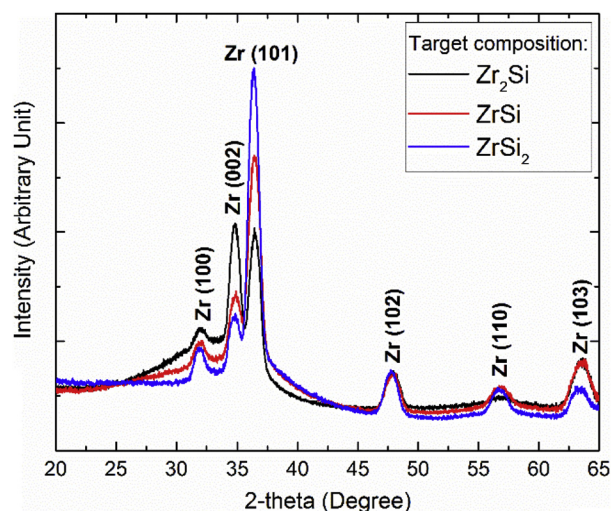


Fig. 1. XRD patterns of thin coatings (Zr₂Si#1, ZrSi#1, and ZrSi₂#1) with 2° incident X-ray beam. Only zirconium peaks from the underlying substrate were identified.

between the long columnar structures at the higher argon pressure may act as paths for the transport of oxygen to the underlying Zirc-4 substrate during the oxidation tests.

The microstructures of the as-deposited coatings were additionally investigated by TEM. The cross-sectional bright field TEM image (Fig. 3a) for the as-deposited ZrSi₂#2 coating displayed a columnar structure defined by the voided boundaries aligned with the film growth direction, but no clear contrast was observed between the grains. Selected area diffraction (SAD) pattern (Fig. 3b) for the corresponding area exhibited diffused halos with fuzzy rings. No distinct diffraction spots characteristic of crystalline phases was observed. Based on XRD patterns and the TEM-SAD analysis, it is speculated that the as-deposited zirconium-silicide coatings are likely amorphous or small volume fraction of nanocrystalline phases in an amorphous matrix. High resolution TEM (HRTEM) images will be required for further analysis of the structure of the as-deposited coatings.

The coating composition, phase content, microstructure, and thickness are summarized in Table 2.

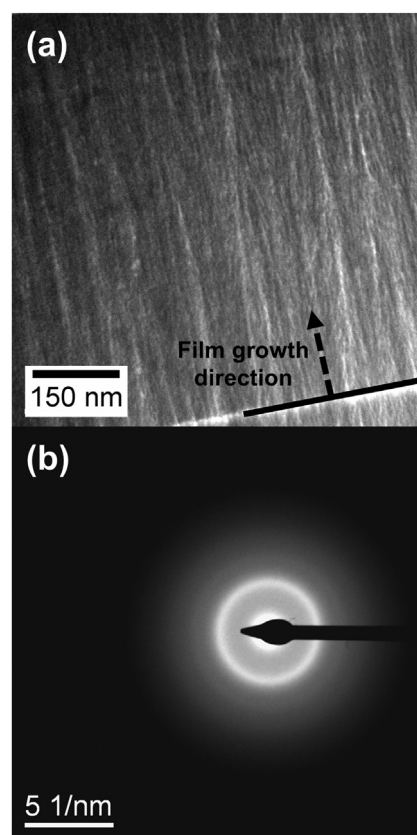


Fig. 3. (a) Cross-sectional bright field TEM image and (b) diffraction pattern of ZrSi₂ #2. The coating of thickness was 3 μm and was prepared by a four-step deposition for the diffraction pattern observation because an electron beam should illuminate the area of interested through the SAD aperture (1 μm diameter). Coating growth direction is indicated by the black dot arrow.

3.2. Oxidation of thin coatings

The thin coatings at lower pressure (Zr₂Si #2, ZrSi#2, and ZrSi₂#2) deposited on Zirc-4 coupons were oxidized at 700 °C for 5 h in ambient air to evaluate their oxidation resistance as a function of coating

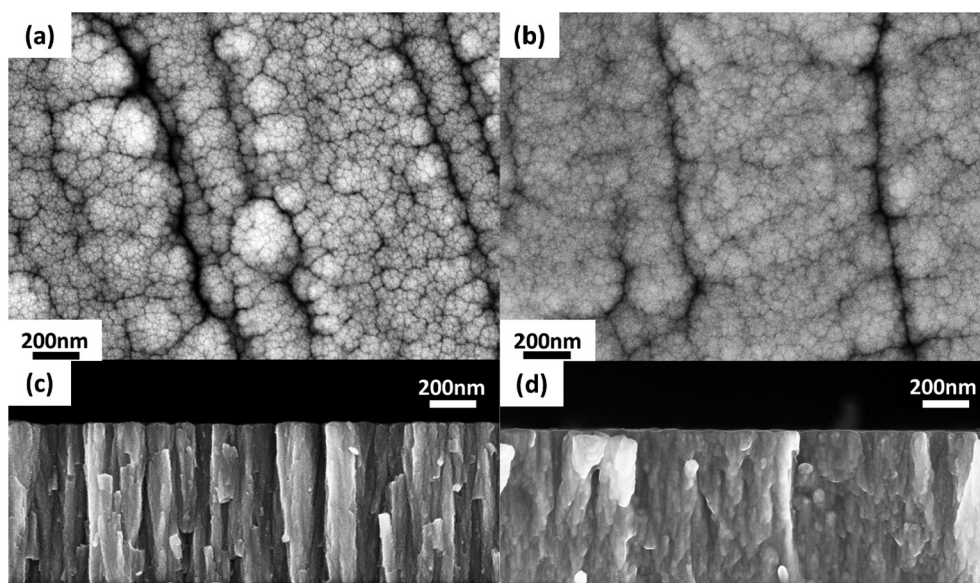


Fig. 2. SEM plan-view images of coatings of (a) ZrSi₂#1 deposited at 1.33 Pa Ar gas pressure and (b) ZrSi₂#2 deposited at 0.53 Pa Ar gas pressure on Zirc-4 substrate. SEM cross-sectional fracture surface images of (c) ZrSi₂#1 deposited at 1.33 Pa Ar gas pressure and (d) ZrSi₂#2 deposited at 0.53 Pa Ar gas pressure on a silicon wafer. The dimensional difference for the microstructure in Fig. 2a and c is attributed to nature and roughness of the substrates. The image in Fig. 2a was from the coating deposited on 600 grit surface finish Zirc-4 substrate while Fig. 2c is the image of the coating deposited on atomically smooth Si wafers.

Table 2

Composition, phase content, microstructure, and coating thickness of the as-deposited thin coatings.

Sample ID	Ar pressure (Pa)	Coating composition	Major structural phase	Microstructure	Thickness (nm)
Zr ₂ Si#1	1.33	Zr _{2.2} Si _{1.0}	Amorphous	Long, tapered, columnar	920
ZrSi#1	1.33	Zr _{1.1} Si _{1.0}	Amorphous	Long, tapered, columnar	870
ZrSi ₂ #1	1.33	Zr _{1.0} Si _{1.9}	Amorphous	Long, tapered, columnar	800
Zr ₂ Si#2	0.53	Zr _{2.2} Si _{1.0}	Amorphous	Short, dense, columnar	800
ZrSi#2	0.53	Zr _{1.0} Si _{1.0}	Amorphous	Short, dense, columnar	750
ZrSi ₂ #2	0.53	Zr _{1.0} Si _{2.2}	Amorphous	Short, dense, columnar	720

stoichiometries. Fig. 4 shows the weight changes (per unit area of the sample) of the coatings of the three stoichiometries and uncoated Zirc-4 at each hour of oxidation. Rapid uptake of oxygen was identified for all the samples during the first hour of exposure, followed by relatively moderate oxidation rate, an effect which is associated with formation of passive oxide layer during the initial exposure, resulting in a self-limiting oxidation behavior. All the coatings revealed smaller weight gain compared to the bare Zirc-4. In particular, the coating with highest Si content (i.e., ZrSi₂#2) displayed the lowest weight gain (about 60% compared to the bare Zirc-4). Since only the two major surfaces of the substrates were primarily coated, the weight gain results underestimate the actual improvements in oxidation resistance of the coatings. Therefore, observation of oxide layer thickness by cross-sectional SEM images was deemed to be a more realistic assessment of the improvements in oxidation behavior due to the coatings.

The thickness of oxide layer of the coatings was measured by cross-sectional SEM images (Fig. 5), and the trends were in good agreement with the weight gain results. Significant oxide layer (13–15 μm) developed underneath the Zr₂Si#2 coating due to permeation of oxygen through the coating and its diffusion into the underlying Zirc-4 substrate. The ZrSi#2 coating appeared to form a thinner zirconium oxide in the underlying Zirc-4 alloy substrate. However, no oxide layer was observed in the underlying Zirc-4 alloy substrate for the ZrSi₂#2 coating. The high magnification images of the oxide scales (Fig. 5d–f) revealed local variation of composition in the thin coatings and substrate. In the upper region of the Zr₂Si#2 and the ZrSi#2 coatings, zirconium-rich oxide was identified by EDS analysis (the brighter regions in Fig. 5d and e), which also contained microcracks which would allow for oxygen permeation to the underlying substrate. However, the oxidized ZrSi₂#2 coating did not show the zirconium-rich oxide in the coating but instead revealed homogenous microstructure. In addition, for the ZrSi₂#2 coating, silicon diffusion from the coating to the substrate was clearly detected which may promote coating-substrate adhesion between the

coating and the substrate. The Si diffusion depth was about 590 nm, and the composition of this region was predominantly ZrSi.

The near-surface chemical composition of the oxidized coatings was analyzed by XPS (signal acquired over a 400 μm diameter circular region) and compositional data is summarized in the Table 3. In all cases the near-surface region showed an enhanced Zr:Si ratio indicating a high inward mobility of silicon in the oxide scale at elevated temperatures.

The binding energy spectrum for O1s in each coating after the oxidation is shown in Fig. 6. The peak binding energy increased with increasing silicon concentration in the coating, which means that characteristics of chemical bonds associated with oxygen were different depending on coating composition. To provide better understanding of the binding energy shift, deconvolution of O1s binding energy for the oxidized coatings was performed via commercial software (Origin 2015). First, the possible binding energy spectrum was assumed to be from three types of potential oxides with Gaussian distribution. The peak energies of these oxides were taken from literature to be, 531.8 eV (ZrSiO₄) [15], 532.4 eV (SiO₂) [16], and 530.5 eV (ZrO₂) [15, 17]. The intensity and FWHM for the components were arbitrarily chosen and iteration using the software was conducted up to the minimum residue between the sum of the estimated oxide spectra and the measured O1s binding energy curve. The deconvolution results indicate the intensity of each oxide component strongly depends on concentration of silicon or zirconium in the coating. The major oxide phase for the zirconium-rich coating (i.e., Zr₂Si#2) was ZrO₂ with minor ZrSiO₄ but that for the silicon-rich coating (i.e., ZrSi₂#2) was SiO₂ with minor ZrSiO₄. The oxidized ZrSi#2 coating showed strong ZrSiO₄ peak with weak ZrO₂ and SiO₂ peaks. The XPS data for the coatings are in good agreement with the pseudo-binary ZrO₂-SiO₂ phase diagram [18]. Theoretically, ZrSiO₄ is the only single stable phase in ZrSi oxidation but compositional alteration (see Fig. 5e) due to the high mobility of silicon may result in ZrO₂ and SiO₂ formation by modulation of activities of zirconium and silicon. In addition, it is speculated that ZrO₂ formation in the coating is one factor that undermines oxidation resistance of the zirconium-silicide coating at elevated temperatures. The weight gain and oxide layer underneath the coatings are proportional to the intensity of ZrO₂ spectrum in the oxidized coating. This is because of relatively higher oxygen transport rate for ZrO₂ through grain boundaries [19] and crack formation in zirconium-rich oxide. However, very low oxygen permeation in SiO₂ [20] and excellent corrosion resistance of ZrSiO₄ [21] appeared to be very beneficial in preventing oxygen permeation to underlying Zirc-4 alloy substrate in high temperature air environment.

Oxidation of the coatings deposited at 1.33 Pa showed larger weight gain and thicker oxide layer than those deposited at 0.53 Pa due to the nanometer scale gaps in the columnar microstructure discussed earlier in Fig. 2. For example, ZrSi₂#2 coating had approximately 59% smaller weight gain compared to ZrSi₂#1 at 700 °C for the 5-hour oxidation test. The studies on these higher Ar gas pressure coatings are not discussed further in this paper.

3.3. Phase stability of thin coatings

One of key properties of an oxidation resistant coating is its thermodynamic stability at elevated temperatures [22]. For example, thermal

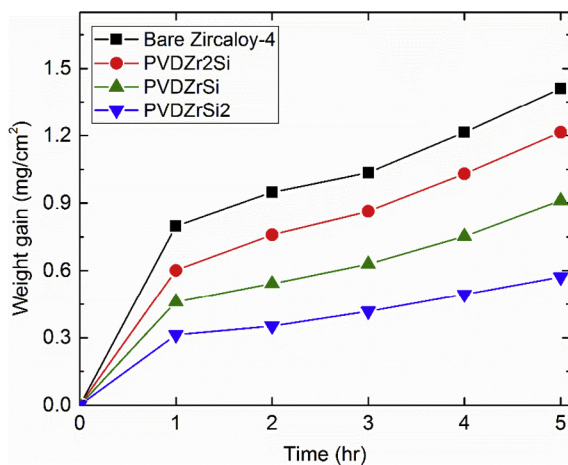


Fig. 4. Weight gain of the zirconium-silicide coatings with different compositions (Zr₂Si#2, ZrSi#2, and ZrSi₂#2) in 700 °C air oxidation test. The coatings were deposited at 0.53 Pa argon pressure.

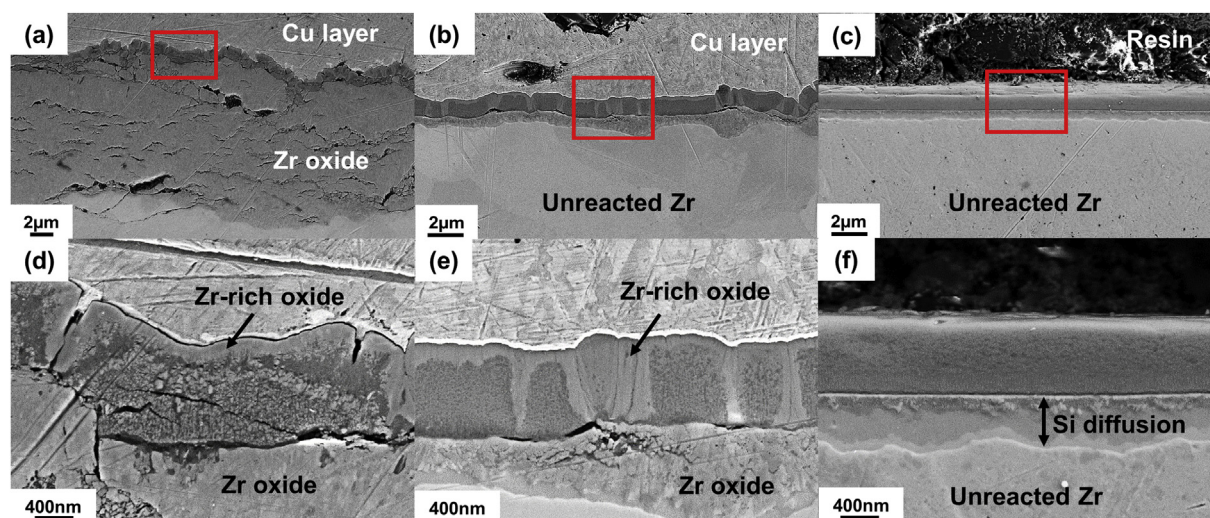


Fig. 5. SEM cross sectional images of (a, d) Zr₂Si#2, (b, e) ZrSi#2, and (c, f) ZrSi₂#2 coatings at low and high magnifications after 700 °C for 5-hour air oxidation test. The high magnification images were acquired in the areas indicated by the red frames in the low magnification images. Cu layer deposited on the coating surface by electroplating to minimize coating damage and edge retention during the sample preparation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

exposure could lead to undesired phase formation in a coating or detrimental chemical interaction between a coating and the substrate. To elucidate the phase stability of zirconium-silicide coatings on Zirc-4 alloy substrate at high temperatures, the thin coatings discussed in the previous section were annealed at 700 °C for 5-hours in an argon environment. High magnification cross-sectional SEM images and zirconium-to-silicon ratio determined by EDS analysis for the coatings (Zr₂Si#2, ZrSi#2, and ZrSi₂#2) after the annealing are shown in Fig. 7.

The Zr₂Si coating showed a local variation of composition but reactivity with the substrate was not distinctively identified based on the SEM image and EDS analysis (Fig. 7a). A decrease in zirconium-to-silicon ratio in the middle of the Zr₂Si coating (indicated by the cross mark in Fig. 7a) was observed. It is believed that residual oxygen inside the quartz capsule reacted with the surface of the Zr₂Si coating, followed by the formation of Zr-rich oxide on the surface. Thus, silicon atoms on the surface diffused inward and increased the Si concentration, however this diffusion was not far enough to reach the substrate. The SEM image of the annealed ZrSi coating displays a thin silicon-rich dark line arising from oxidation-induced silicon diffusion from the surface and silicon diffusion zone in the substrate (Fig. 7b). It is worth noting that a network of micron-scale cracks in the annealed Zr₂Si and ZrSi coatings was observed as shown in Fig. 7c. The cracks appeared to initiate from conical-shaped defects which propagated to the substrate. It is expected that oxygen would readily permeate the coating through the open gap around these defects at elevated temperatures, resulting in reduced oxidation resistance. The annealed ZrSi₂ coating showed silicon diffusion to the substrate similar to the oxidized ZrSi₂ coating discussed earlier but the diffusion depth was smaller (~310 nm) than the air-oxidized samples (~590 nm), indicating that surface oxidation also drives Si inward towards to the coating-substrate interface. One plausible explanation is that oxidation generates additional unbound silicon atoms in oxide scale, which is supported by a previous study [8] - bulk ZrSi₂ oxidation at 700 °C in ambient air produced a solid state mixture Zr-Si-O

and a silicon phase. The newly released free silicon atoms showed a high diffusivity, and were associated with evolution of complex microstructures. In addition, XRD analysis for the annealed coatings showed not only strong zirconium peaks from the substrate but also weak zirconium-silicide peaks, indicating initiation of crystallization of the coatings.

In summary, the annealing experiments confirmed compositional alteration of zirconium-silicide coatings (Zr₂Si, ZrSi, and ZrSi₂) on Zirc-4 substrate at 700 °C mainly due to the mobility of silicon atoms in the coatings followed by the reaction with the substrate.

3.4. Oxidation resistance of optimized ZrSi₂ coatings

Based on the oxidation and annealing of the thin zirconium-silicide coatings at 700 °C for 5 h discussed above, silicon-rich zirconium-silicide stoichiometry, ZrSi₂, was selected as a potential oxidation resistant coating for Zirc-4. For this next phase of the study, a thicker optimized zirconium-silicide coating (ZrSi₂#3) was prepared by six deposition steps under 0.53 Ar pressure.

A cross-sectional SEM in-lens image for the optimized coating is shown in Fig. 8a. The coating thickness was approximately 3.9 μm. The coating displayed dense and columnar microstructure similar to those observed in the thin ZrSi₂ coatings (Fig. 2d) and the interface between each deposition step was revealed as the faint horizontal lines. No spallation or cracks were identified. To evaluate oxidation resistance of the optimized coating, three oxidation experiments were conducted: 1) 700 °C for 20 h, 2) 1000 °C for 1 h, and 3) 1200 °C for 10 min.

The longer oxidation for the coating at 700 °C enabled us to better understand oxide scale growth on the coating and phase stability in the coating/substrate interface. The samples were heated up to 700 °C with slow ramp rate (5 °C/min) and the temperature was maintained for 20 h. As shown in Fig. 8b, oxygen permeation through the coating was significantly mitigated and the thin oxide layer of thickness of 750 nm formed on the top surface of the coating during the 20-hour oxidation. In contrast, the bare Zirc-4 substrate developed about a 65 μm thick oxide layer. This suggests that oxidation resistance factor of improvement of the coating is more than 85 compared to bare Zirc-4 at 700 °C air. The very near-surface atomic percent of the oxide layer was 14%-Zr, 19%-Si, and 66%-O as measured by XPS (see Table 4) and corresponding binding energy spectra are identical to those of thin ZrSi₂ layer (ZrSi₂#2) after the 700 °C for 5-hour air oxidation. The protective nature for the coating is mainly attributed by the SiO₂ and ZrSiO₄ oxide layer.

Table 3

XPS compositional analysis of the coatings after 700 °C for 5-hour air oxidation. Numbers are in atomic percent for each element on the surface. The last column indicates the atomic percent ratio of zirconium and silicon.

Sample ID	Si2p	Zr3d	O1s	C1s	Zr: Si
Zr ₂ Si#2	8.05	22.25	64.59	5.11	2.8:1.0
ZrSi#2	12.30	18.88	65.65	3.17	1.5:1.0
ZrSi ₂ #2	17.92	13.09	63.64	5.34	1.0:1.4

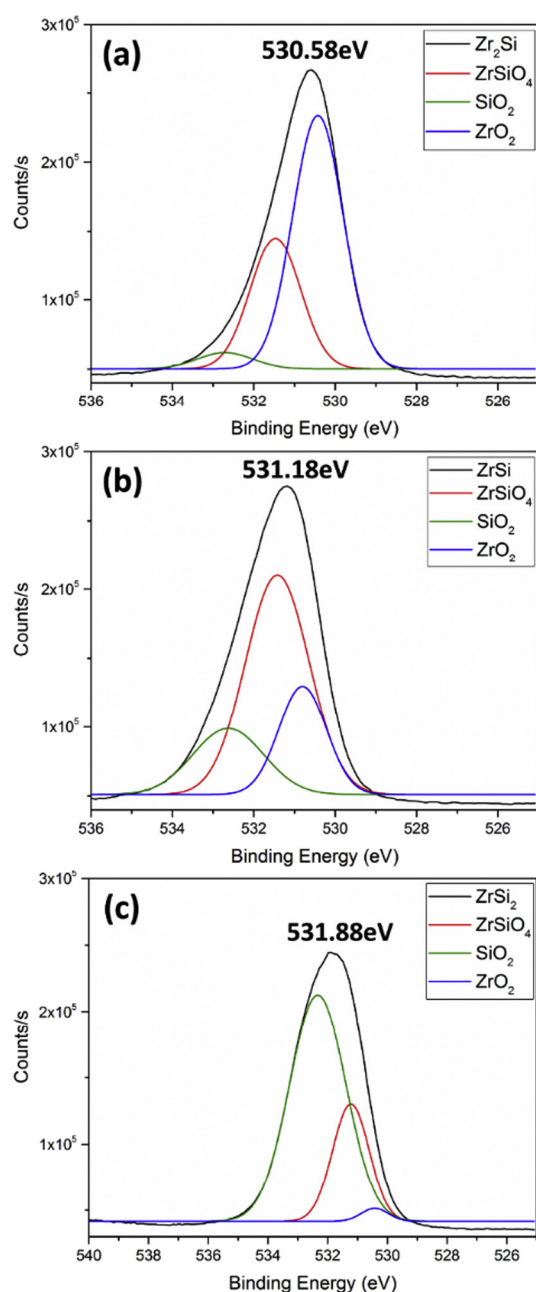


Fig. 6. XPS O1s spectra of zirconium-silicide coatings after 700 °C for 5-hour oxidation: (a) Zr₂Si#2, (b) ZrSi#2, and (c) ZrSi₂#2. The O1s spectra were resolved into possible oxide components (red curve: ZrSiO₄, green curve: SiO₂, and blue curve: ZrO₂). The measured spectrum is indicated by dark curve. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The XRD pattern (Fig. 8c) revealed not only ZrSi₂ arising from crystallization of the unreacted coating and zirconium substrate peaks, but also a broad halo in the range of 24° to 30° in 2θ. Possible phases for the broad hump are ZrSi₂, SiO₂ (quartz), and ZrSiO₄ listed as follows: ZrSi₂ (040) at 24.05°, ZrSi₂ (021) at 24.79°, ZrSi₂ (130) at 30.19°, SiO₂ (011) at 25.16°, SiO₂ (220) at 28.41°, SiO₂ (310) at 28.48°, and ZrSiO₄ (200) at 26.67°. The XRD pattern would be a superposition of the nanocrystalline phases and amorphous phase, assuming that nanocrystalline phases (ZrSiO₄, SiO₂, and ZrSi₂) were precipitating in amorphous oxide matrix in the progress of 700 °C oxidation. The phase of the thin protective oxide layer is also consistent with an oxide layer formed on bulk ZrSi₂ in 700 °C in ambient air [8]. In addition, the silicon diffusion zone

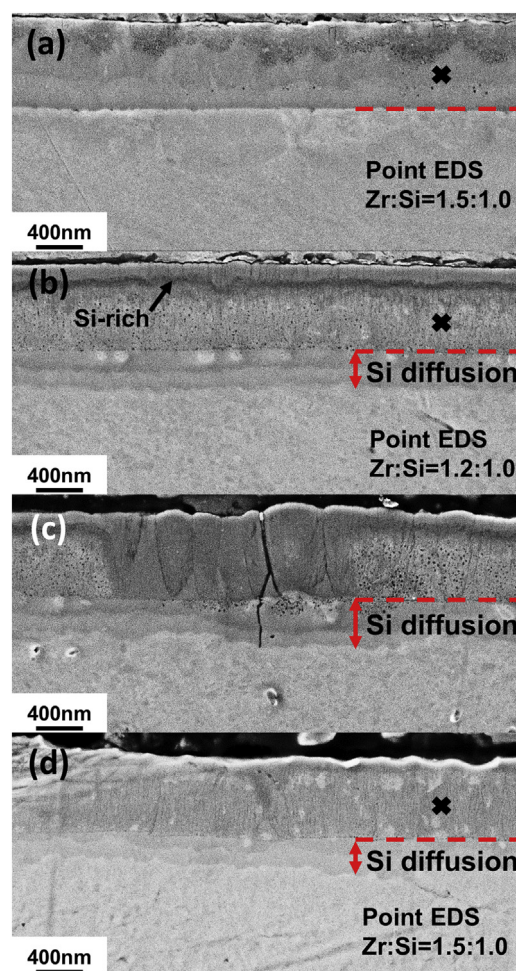


Fig. 7. SEM cross-sectional images of annealed (a) Zr₂Si#2, (b, c) ZrSi#2, and ZrSi₂#2 at 700 °C for 5 h in argon gas. Interface between the coating and the substrate and silicon diffused zone are indicated by the red dot line and red arrow, respectively. A ratio of zirconium-to-silicon at the dark cross is stated on each figure, measured by EDS point scan analysis. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

into the Zirc-4 alloy of thickness of 630 nm was identified. Interestingly, the silicon atoms were supplied from about 1.4 μm of the ZrSi₂ coating contacting with the substrate because the region displayed silicon reduction (ZrSi₂ → ZrSi_{1.5}) and formation of nano-scale pores due to clustering of vacancies from the substitutional diffusion of Si (dark spots in Fig. 8b).

The high temperature oxidation tests for the optimized coatings were conducted at 1000 °C for 1 h and 1200 °C for 10 min. For these tests, the coated samples were inserted directly in a pre-heated furnace resulting in a rapid heating rate. After the exposure, the samples were air-cooled to room temperature. These tests demonstrated material degradation due to oxidation and thermal shock. For these tests, two types of samples were evaluated, (i) as-deposited coating and (ii) after pre-oxidation at 700 °C air for 5 h. The pre-oxidation condition was the same as was used for the oxidation tests used for thin coatings discussed earlier. Thus the pre-oxidized samples used for the 1000 °C and 1200 °C would have the same submicron thickness protective oxide layer. As shown in Fig. 9a and b, significant differences in surface morphology between the as-deposited coating and the pre-oxidized coating were observed after the 1000 °C oxidation. Micron-scale cracks were observed (Fig. 9a) on the entire area of the as-deposited coating, indicating the coating did not provide the necessary oxidation

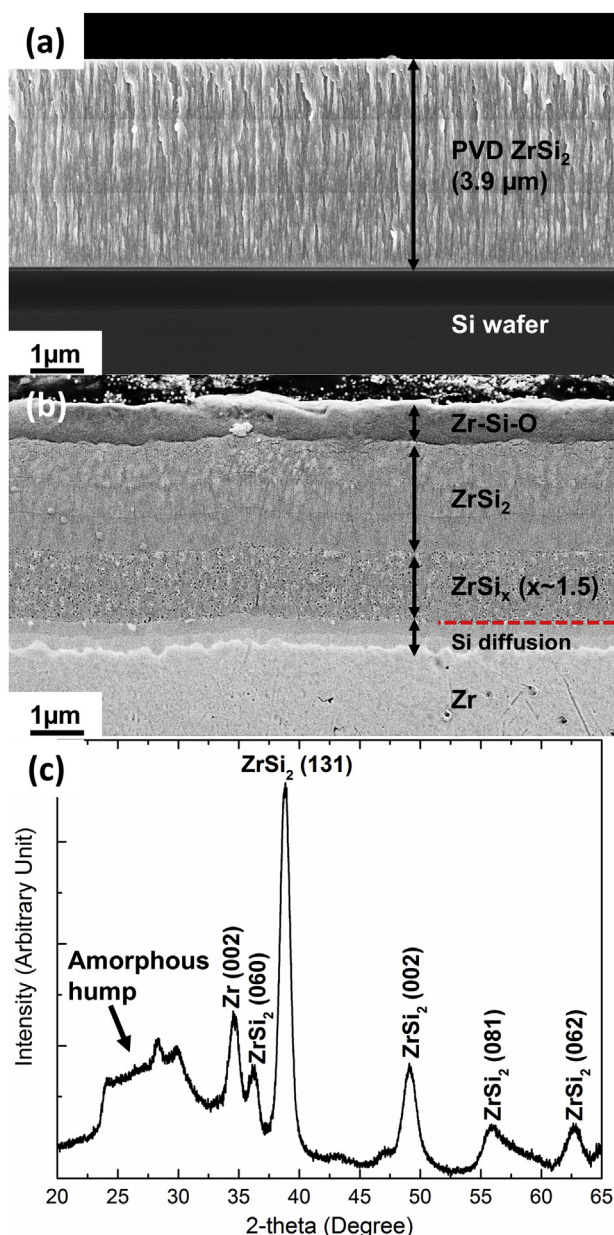


Fig. 8. SEM cross-sectional images of (a) as-deposited ZrSi_2 coating ($\text{ZrSi}_2\#3$) on silicon wafer and (b) oxidized ZrSi_2 coating on Zirc-4 at 700 °C for 20 h. Interface between the coating and the substrate is indicated by the red dots. (c) XRD pattern for the oxidized ZrSi_2 on Zirc-4 at 700 °C for 20 h. The dark arrow in Fig. 8c points to broad halo associating with the thin oxide layer in Fig. 8b. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

resistance. The degradation of the as-deposited coating might be explained by the absence of the protective oxide layer and loss of thermal stability of the coating. A sudden temperature surge to 1000 °C in air produced ZrO_2 on the surface due to silicon inward diffusion rather

Table 4

XPS compositional analysis of the optimized coatings ($\text{ZrSi}_2\#3$) after the oxidation tests. The numbers are in atomic percent of each element on the very near-surface. The last column shows the atomic percent ratio of zirconium and silicon.

Oxidation test	Si2p	Zr3d	O1s	C1s	Zr: Si
700 °C for 20 h	18.82	13.63	65.50	2.06	1.0:1.4
1000 °C for 1 h	15.06	17.88	64.78	1.67	1.2:1.0
700 °C for 5 h → 1000 °C for 1 h	17.24	14.40	67.07	1.30	1.0:1.2
700 °C for 5 h → 1200 °C for 10 min	15.99	15.10	67.68	1.23	1.0:1.1

than formation of the Zr-Si-O protective oxide layer. As discussed in the previous section, silicon diffusion from the ZrSi_2 coating to Zirc-4 substrate was identified at 700 °C in both oxidation and annealing. Increase of Zr-to-Si ratio on the oxidized surface at 1000 °C without the pre-oxidation as confirmed in XPS analysis (Table 4), and the local silicon rich area in the cross-sectional image of the coating (Fig. 9c) also support this explanation. According to the diffusion couple experiments between Ti_3SiC_2 and Zirc-4 [23], the effective diffusion coefficient of Si in Zirc-4 at 1300 °C was approximately six times larger than that at 1100 °C. Therefore, remarkably rapid silicon loss of the coating, which accelerated by the surface oxidation at 1000 °C in the absence of the protective layer, generated microstructural defects (i.e., clusters of voids) in the coating, which induced the crack formation and intensified the material degradation. On the other hand, not only no noticeable defects such as delamination, cracks, or spallation but also higher silicon concentration compared to zirconium on the very near-surface was observed on the pre-oxidized coating surfaces with the 1000 °C and 1200 °C exposures.

The protective nature of the top oxide layer formed on the pre-oxidized sample was also confirmed in the cross-sectional SEM image of the sample after the 1000 °C and 1200 °C oxidation tests (Fig. 10). After oxidation at 700 °C for 5 h followed by the 1000 °C for 1 h, total thickness of the oxide scale for the coating was about 7 μm, but that of the bare Zirc-4 oxidized at the same condition was about 89 μm. However, the as-deposited coating (i.e., without pre-oxidation) after the test had thicker oxide scale (approximately 106 μm) than the bare Zirc-4, resulting from oxygen ingress through the cracks as observed in Fig. 9a and c. The oxygen penetration depth for the pre-oxidized coating after the 1000 °C test was also measured by EDS line scan analysis as shown in Fig. 10b. The pre-conditioning produced about 730 nm thickness oxide layer on the top, ZrO_2 (~6.3 μm), ZrSi_2 (~0.9 μm), and ZrSi layer (~3.5 μm) subsequently. In addition, the oxide layer thickness of the pre-oxidized coating after the 1200 °C test was about 20 μm, which was nearly one tenth of oxide scale of the bare Zirc-4 (about 208 μm) at the condition. The oxide scale for the coated samples consisted of thin protective layer (750 nm) on the top, thick ZrO_2 layer (~17 μm), ZrSi_2 islands, and ZrSi layer (~2.3 μm). Interestingly, the protective oxide layer formed on the pre-oxidation (700 °C) transformed to nanoscale ZrO_2 phase particulates and SiO_2 matrix at the 1000 °C and 1200 °C exposures as shown in Fig. 10c and d. The microstructure was not identified in the oxide scale at 700 °C (Figs. 5f and 8b).

The phase transformation from the Zr-Si-O oxide mixture to the ZrO_2 and SiO_2 phase was also reported in annealing of mixture of ZrO_2 and SiO_2 thin film at 900 °C for 60 s [24] and oxidation of bulk ZrSi_2 at 1000 °C and 1200 °C for 5 h in ambient air [8]. The authors suggested that a thermodynamic driving force exists in disordered Zr-Si-O mixture, leading to nucleation and growth of ZrO_2 in SiO_2 matrix instead of formation of ZrSiO_4 . During the pre-conditioning, the oxide layer consisting of a mixture of the nanocrystalline phases and amorphous phase generates, which might heal inherent microstructural defects (i.e., conical defects) so that the oxide layer hindered oxygen permeation during the 1000 °C and 1200 °C oxidation. In addition, the multi-layered scale structure at the high temperatures evolves due to slow oxidation kinetics arising from the thin protective layer. The partial pressure for oxygen might be significantly decreased in the protective layer, resulting in a slower oxidation process of the rest of the ZrSi_2 coating. In the meantime, the silicon in the coating migrated inward to the substrate, increasing activity of zirconium. The mobile silicon atoms reacted with the substrate and formed the ZrSi_2 and ZrSi layers, which is supported by the zirconium-silicon diffusion couple experiments at 900 °C to 1400 °C in inert environments. Bertolino et al. [25] reported formation of the ZrSi_2 and ZrSi layers in the conditions. When oxygen diffused through the protective layer and reacted with zirconium atoms, the ZrO_2 scale was formed. Lastly, it is expected that oxidation of the ZrSi_2 coating with the pre-oxidation at even higher temperatures (e.g., 1300 °C or 1400 °C) produces micron-grained ZrSiO_4 phase in the

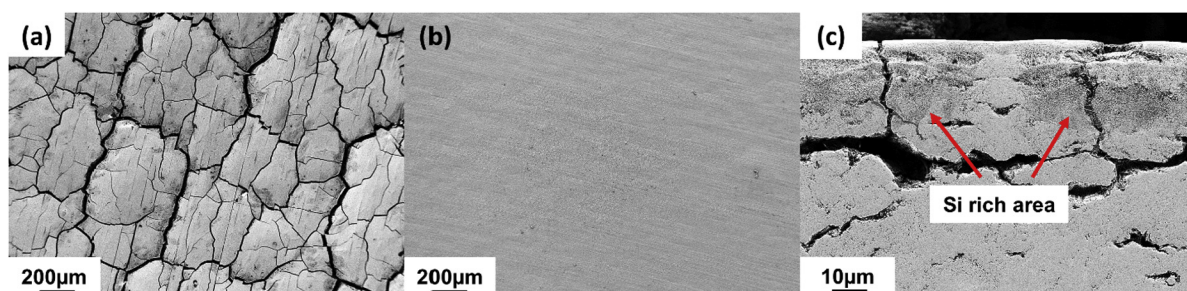


Fig. 9. SEM plan-view images of (a) $\text{ZrSi}_2\#3$ oxidized at 1000 °C for 1 h, (b) $\text{ZrSi}_2\#3$ with pre-oxidation (700 °C for 5 h) oxidized at 1000 °C for 1 h, and (c) Cross-sectional image of $\text{ZrSi}_2\#3$ oxidized at 1000 °C for 1 h, showing cracks and Si rich area in the thick oxide scale. The samples were rapidly heated up to the high temperature air. After the exposure, the coating was air-cooled to room temperature.

protective layer by solid state reaction of the ZrO_2 particulates and the SiO_2 matrix, which would provide enhanced oxidation resistance [26].

4. Conclusions

Optimization of zirconium-silicide coating on Zircaloy-4 substrate prepared by a magnetron sputter deposition was investigated to improve oxidation resistance in a high temperature air environment. Three coating stoichiometries, namely, Zr_2Si , ZrSi , and ZrSi_2 were deposited at room temperature showed columnar structures. Coating composition and argon pressure during deposition were adjusted to attain minimal weight gain and oxygen penetration at 700 °C air. Initial air-oxidation tests at 700 °C air for 5 h showed the ZrSi_2 coating deposited at 0.53 Pa to have the best oxidation resistance due to a denser microstructure and formation of a protective oxide layer. It is speculated that the

oxidation resistance of the protective layer is attributed to the nanocrystalline SiO_2 and ZrSiO_4 phases in the amorphous matrix. SEM-EDS examination indicated ready mobility of Si outward to form an oxide and inward to form an intermetallic compound with the Zircaloy-4 substrate. Thicker ZrSi_2 coating (3.9 µm) was synthesized using these optimized parameters. The thicker coatings showed improvement of almost two orders of magnitude when compared to bare Zircaloy-4 after air-oxidation at 700 °C for 20-hours. Pre-oxidation of ZrSi_2 coating at 700 °C for 5 h significantly mitigated oxygen diffusion in air-oxidation tests at 1000 °C for 1-hour and 1200 °C for 10-minutes; the total oxide layer thickness for 1000 °C and 1200 °C tests to be only 7 µm and 20 µm, respectively. On the other hand, the bare Zircaloy-4 showed 89 µm and 208 µm oxide scale thickness, respectively, under these oxidation test conditions. No spallation or cracks were observed in the ZrSi_2 coating due to air cooling to room temperature after high temperature

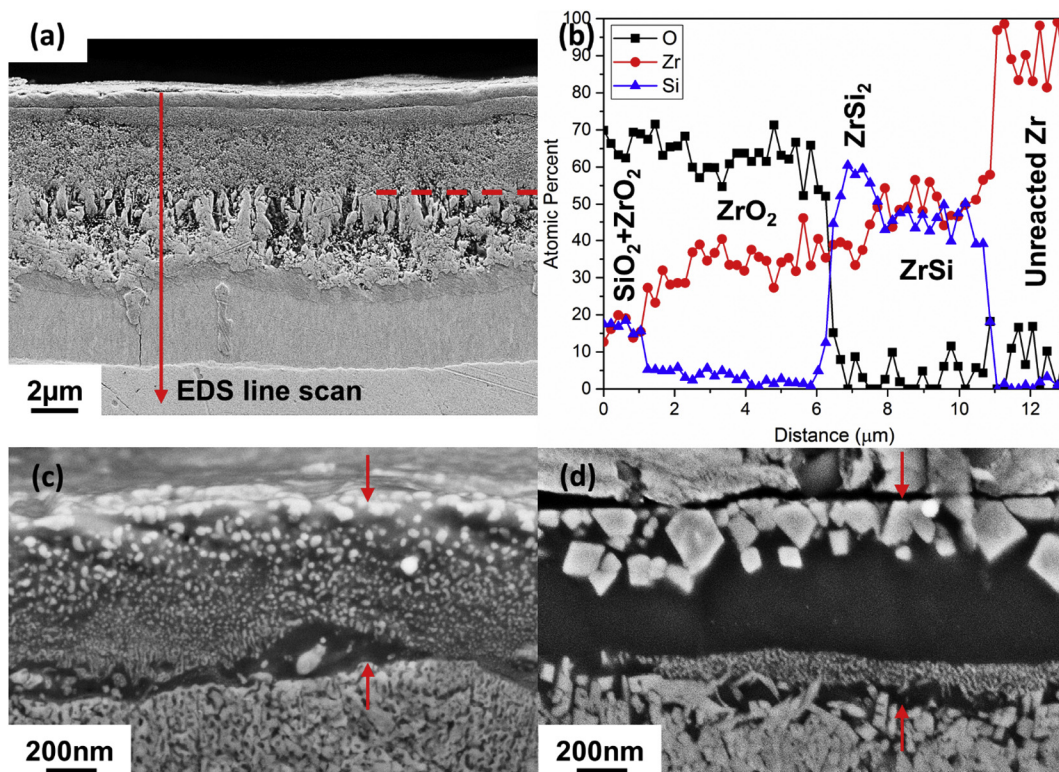


Fig. 10. SEM cross-sectional images and EDS line scan of $\text{ZrSi}_2\#3$ with the pre-oxidation after the 1000 °C for 1-hour air oxidation: (a) Low magnification and (b) EDS line scan result corresponding to Fig. 9a. The red dots and the red solid arrow in Fig. 9a refers to interface between the coating and substrate and the EDS scan direction, respectively. High magnification cross-sectional SEM images of top surface of the pre-oxidized coatings after (c) the 1000 °C for 1 h and (d) the 1200 °C for 10 min. The red solid arrows in Fig. 9c and d refer to the thin protective layer consisting of nanoscale ZrO_2 phases in SiO_2 matrix. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

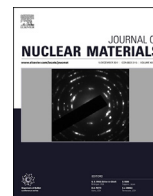
oxidation tests. The results of this initial study suggest that the ZrSi₂ coating could be a good candidate coating for protection Zr-alloy (or other substrates) under air oxidation conditions.

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Evaluation of steam corrosion and water quenching behavior of zirconium-silicide coated LWR fuel claddings

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HIGHLIGHTS

- Steam corrosion testing (400 °C steam and 10.3 MPa for 72 h) led to weight loss of ZrSi₂ and Si.
- Pre-oxidation of ZrSi₂ coating on Zircaloy-4 at 700 °C air for 5 h mitigated corrosion process.
- ZrSiO₄ phase, formed by exposing ZrSi₂ coating on SiC at 1400 °C in air, immobilized silicon in the steam condition.
- Water quenching heat transfer was improved by ZrSi₂ coating on Zircaloy-4.

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ABSTRACT

This study investigates steam corrosion of bulk ZrSi₂, pure Si, and zirconium-silicide coatings as well as water quenching behavior of ZrSi₂ coatings to evaluate its feasibility as a potential accident-tolerant fuel cladding coating material in light water nuclear reactor. The ZrSi₂ coating and Zr₂Si-ZrSi₂ coating were deposited on Zircaloy-4 flats, SiC flats, and cylindrical Zircaloy-4 rodlets using magnetron sputter deposition. Bulk ZrSi₂ and pure Si samples showed weight loss after the corrosion test in pure steam at 400 °C and 10.3 MPa for 72 h. Silicon depletion on the ZrSi₂ surface during the steam test was related to the surface recession observed in the silicon samples. ZrSi₂ coating (~3.9 μm) pre-oxidized in 700 °C air prevented substrate oxidation but thin porous ZrO₂ formed on the coating. The only condition which achieved complete silicon immobilization in the oxide scale in aqueous environments was the formation of ZrSiO₄ via ZrSi₂ coating oxidation in 1400 °C air. In addition, ZrSi₂ coatings were beneficial in enhancing quenching heat transfer - the minimum film boiling temperature increased by 6–8% in the three different environmental conditions tested. During repeated thermal cycles (water quenching from 700 °C to 85 °C for 20 s) performed as a part of quench tests, no spallation and cracking was observed and the coating prevented oxidation of the underlying Zircaloy-4 substrate.

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1. Introduction

Zirconium-alloy (Zr-alloy) fuel claddings have been widely used in light water nuclear reactor (LWR) for several decades due to their excellent neutron transparency and combination of corrosion resistance and mechanical properties in normal operation conditions [1]. However, since the Fukushima accident in 2011,

performance issues of the typical UO₂ – Zr-alloy fuel system under design-based and beyond-design basis accident scenarios have been highlighted. Under an accident scenario with a limited cooling capability to a reactor core, the fuel temperature increases rapidly due to decay heat and the remaining coolant boils. Under the condition, Zr-alloy cladding reacts with high temperature steam exothermically, leading to the loss of intrinsic mechanical properties for retention of radioactive materials because of oxide layer formation and hydrogen embrittlement [2–4]. The issues have motivated innovative approaches in development of accident tolerant fuels (ATF) that can tolerate high temperatures for longer times than the conventional fuel system, so as to increase coping

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time during possible accident scenarios. Leading nuclear industries, universities, and national laboratories are investigating various ATF concepts. Major approaches to enhance the safety margin of LWR fuels are as follows: development of alternative fuel cladding material as complete replacement of Zr-alloy cladding such as FeCrAl alloy [5,6] and SiC-SiC composites [4,7] and a fabrication of protective coatings on Zr-alloy cladding surface including chromium [8,9], FeCrAl [10], ZrSi₂ [11], Ti₂AlC [12,13], and TiN [14] coatings. The deposition of oxidation resistant coatings on the Zr-alloy surface has been investigated as a short-term solution with the advantage of being compliant with the current reactor core designs. In addition, recent studies on modified surfaces for boiling heat transfer enhancement provides a basis for an optimal design of coated Zr-alloy claddings [15–17]. Boiling heat transfer characteristics of accident tolerant coated claddings must be evaluated in parallel. The assessment of thermal-hydraulics is essential for understanding the role of ATF cladding design on heat transfer behavior. For example, critical heat flux and minimum film boiling temperature for ATF claddings under various reactor operating conditions would be important metrics to establish the thermal limits that define nuclear reactor safety margins and provide a measure of cooling performance of safety systems in LWRs.

Transition-metal silicide compounds (e.g. MoSi₂, TiSi₂) have been widely used in high temperature applications due to its superior oxidation resistance, low density, and excellent mechanical properties [18,19]. Of the transition metal silicide candidate coatings for the cladding application, zirconium-silicide appears to be the most logical choice from the standpoints of neutronics and superior compatibility with zirconium-alloy substrate. Zirconium-silicide intermetallic compounds have high melting points [20]; Zr₂Si, ZrSi, and ZrSi₂ are stable up to 1927 °C, 2203 °C, and 1626 °C, respectively. Application of zirconium-silicide coating on the surface of Zr-alloy is reasonable because of similarities in linear thermal expansion coefficient and inherent compositional compatibility between the coating and the substrate [21,22]. Finally, the formation of a tenacious oxide layer, consisting of multilayered ZrO₂ and SiO₂ structures could provide radiation damage tolerance in high dose conditions, and a highly corrosion resistant material, zircon (ZrSiO₄) can be intrinsically produced at high temperatures [23]. For example, optimized magnetron sputter ZrSi₂ coatings in the previous study showed oxidation resistance for Zircaloy-4 substrate at 700 °C, 1000 °C, and 1200 °C air conditions [11]. Experimental corrosion data of zirconium-silicide compounds and coated Zr-alloy substrates in aqueous environments provide a basis for the material behavior under normal operating conditions in LWRs. Furthermore, there are no previous studies on quenching performance for zirconium-silicide coated Zr-alloy in a water pool, evaluating the cooling ability and robustness of the coating. This type of test simulates activation of emergency core cooling system (ECCS) injection in accident scenario.

To evaluate the feasibility of zirconium-silicide coatings as a potential ATF coating material, pressurized steam tests for bulk zirconium-silicide, silicon, and zirconium-silicide coatings with various architectures prepared by magnetron sputter deposition were investigated. The samples were exposed to 400 °C steam and 10.3 MPa for 72 h and were characterized to quantify any alterations in surface morphology, composition, and thickness of oxide scale. In addition, thin ZrSi₂ coatings were deposited on cylindrical Zircaloy-4 rodlets, and transient boiling heat transfer during a rapid quenching under saturated, subcooled, and pressurized water conditions were explored. Temperature history at a center of the test section was measured and boiling visualization was performed during the quenching experiments. Coating damage effects such as cracking, delamination, and surface oxidation during the rapid quenching were characterized, and effect of the ZrSi₂ coating on

quenching performance is discussed in detail.

2. Experimental

2.1. Materials and coating deposition

Bulk ZrSi₂ and single crystal pure silicon coupons were used for steam corrosion tests, which were purchased from American Elements Inc. (Los Angeles, CA) having a purity of >99.5% and SCI Engineered Materials (Columbus, OH), respectively. The phases in the as-received materials were confirmed by x-ray diffraction analysis (XRD), but few micron-sized free Si particle impurities were detected in the matrix of as-received ZrSi₂. Zr-alloy plates (Zircaloy-4 grade: 0.07 wt% Cr, 0.18 wt% Fe, 0.09 wt% O, and balanced Zr) were procured from ATI Wah Chang (Albany, OR), and commercially available Moissanite 3C (β) CVD SiC flats were purchased, which both flats were used as substrates for zirconium-silicide coatings. The bulk materials were sectioned to square samples approximately 12.7 × 12.7 mm², 2.8 mm thick in dimensions. The samples were then ground with 320 grit and 600 grit SiC abrasive papers followed by ultrasonic cleaning in acetone and ethanol baths for 20 min each. The samples were then fully dried under airflow in room temperature. For magnetron sputter deposition on the Zircaloy-4 (Zirc-4) substrate, zirconium-silicide intermetallic compounds (i.e. ZrSi₂ and Zr₂Si) sputter targets were procured from American Elements Inc. The target materials with 99.5% nominal purity had dimensions of 76 mm in diameter and 3.2 mm in thickness. The targets had 3.2 mm thick copper backing plates for preventing fracture due to a thermal shock during the deposition process. For preparing quench test specimens, 300 mm-length Zirc-4 rods were purchased from Eagle alloys corp. (Talbott, TN) and were machined to short rodlets having dimension of 50 mm in length and 10 mm in diameter.

The zirconium-silicide coatings were deposited on Zirc-4 flats, SiC flats, and Zirc-4 rodlets using magnetron sputter deposition technique. In this process, glow discharge Ar plasma bombards the zirconium-silicide target and the sputtered target atoms condense on the substrate to be formed a thin film. The deposition process was performed under 138 W DC power, 0.53 Pa argon gas pressure, no substrate heating (19 °C), and a rotating sample stage (10 rpm). Detailed procedure and conditions for the deposition is described in the previous work [11]. To achieve thicker coatings and compositional layered coatings, multiple deposition was conducted. A plasma cleaning step (DC 500 W for 5 min in 1.6 Pa Ar pressure) was employed between each deposition step to remove surface contamination due to the interruptions in the coating process. For holding the rod samples during the deposition, small aluminum plates were machined to have a single rectangular channel of 3.2 mm in width as shown in Fig. 1a. The rod samples fixtured on the short plates were placed on the sputter stage in the vacuum chamber. The rodlets were flipped over 180° after the first deposition, improving uniformity of the deposition. The coated samples showed a slight thickness variation in circumferential measurements; thickness difference between the maximum and the minimum thickness was approximately 0.4 μm. Fig. 1b shows the ZrSi₂ coated Zirc-4 rodlets with 316 stainless tube extension for quenching experiments.

2.2. Steam corrosion test

Isothermal corrosion tests in pressurized steam, simulating corrosion of materials in LWR operating environment, were performed for the bulk and coated samples. The high-temperature autoclave used for steam corrosion testing had a diameter of 40 mm and a length of 508 mm. The test section was made of

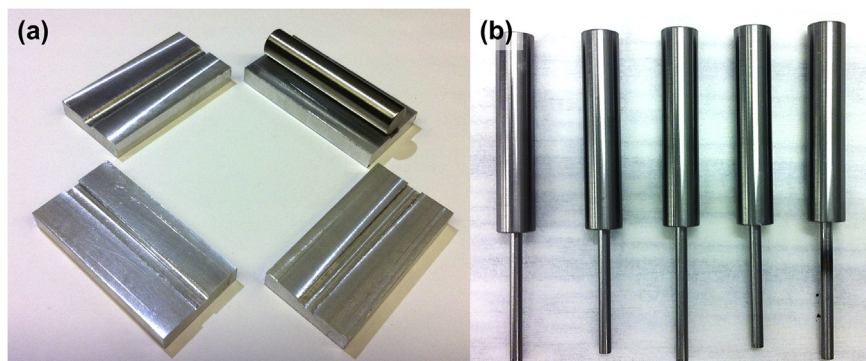


Fig. 1. Photograph of (a) a cylindrical Zirc-4 sample on the short aluminum plates and (b) ZrSi_2 thin coating on the Zirc-4 samples with the stainless-steel tube extensions.

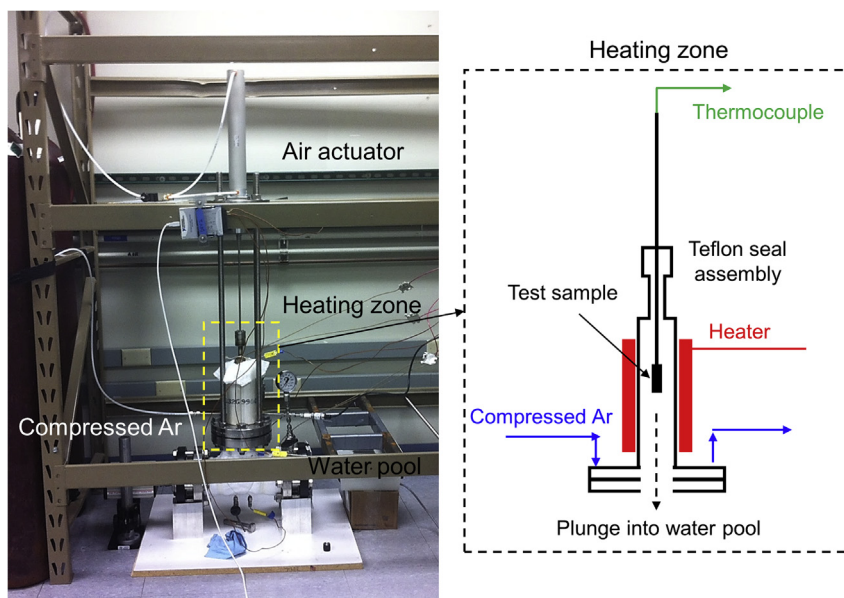


Fig. 2. Photograph of the quench test facility and schematic illustration of the heating zone.

nickel-based alloy 625 and the samples were mounted onto a holder, also made of Alloy 625, with electrical isolation being achieved by using alumina washers between the samples and sample holder. Test conditions were high temperature steam ($400\text{ }^{\circ}\text{C}$) and 10.3 MPa for 72 h. Deionized pure water (18 M Ω cm) was flowed into the autoclave with a slow flow rate (approximately 5 ml/min). The experimental uncertainty of the temperature and pressure in the test section were $\pm 1\text{ }^{\circ}\text{C}$ and $\pm 0.2\text{ MPa}$, respectively.

Weight gain measurements were performed for the bulk materials after steam exposure as an initial measure of corrosion and this measurement had an uncertainty of 0.002 mg. Corrosion of the materials in regards to surface morphologies and cross-sectional microstructure were investigated by Zeiss LEO Scanning Electron Microscope (SEM) in conjunction with X-ray energy dispersive spectroscopy (EDS). Phase identification of corrosion products was performed using Bruker D8 Discovery X-ray diffraction (XRD) with

Table 1

Summary of sample composition, geometry, and experimental conditions used in this study.

Sample ID	Sample description [coating thickness]	Experimental conditions
Zirc-4	Bulk Zirc-4	Steam corrosion
ZrSi ₂ #1	Bulk ZrSi ₂	Steam corrosion
ZrSi ₂ #2	Bulk ZrSi ₂	700 $^{\circ}\text{C}$ in air for 100 h $\rightarrow$ steam corrosion
Si#1	Bulk silicon	Steam corrosion
Si#2	Bulk silicon	700 $^{\circ}\text{C}$ in air for 100 h $\rightarrow$ steam corrosion
Si#3	Bulk silicon	1400 $^{\circ}\text{C}$ in air for 5 h $\rightarrow$ steam corrosion
CZrSi#1	ZrSi ₂ [3.9 μm] on flat Zirc-4	Steam corrosion
CZrSi#2	ZrSi ₂ [3.9 μm] on flat Zirc-4	700 $^{\circ}\text{C}$ in air for 5 h $\rightarrow$ steam corrosion
CZrSi#3	Outer Zr ₂ Si [3 μm] + Inner ZrSi ₂ [3 μm] on flat Zirc-4	Steam corrosion
CZrSi#4	Outer Zr ₂ Si [3 μm] + Inner ZrSi ₂ [3 μm] on flat Zirc-4	400 $^{\circ}\text{C}$ in air for 10 h $\rightarrow$ steam corrosion
CZrSi#5	ZrSi ₂ [3 μm] on flat SiC	1400 $^{\circ}\text{C}$ in air for 5 h $\rightarrow$ steam corrosion
CZrSi#6	ZrSi ₂ [2.1 μm] on cylindrical Zirc-4	Water quenching

Cu K α radiation and diffraction peaks were acquired from 30° to 90° with coupled 2 θ mode and from 30° to 50° in 2 θ with a 2° grazing incident beam.

2.3. Quench experiments

Quenching experiments for the ZrSi₂ coated Zirc-4 samples, simulating sudden reflood of the overheated fuel rod in an accident scenario, were performed in the deionized water pool under three environmental conditions: atmospheric saturated water, saturated water at 0.5 MPa, and subcooled water (85 °C) at atmospheric pressure. Fig. 2 shows the experimental system for the quench test, consisting of the air actuator, the heating zone, and the water pool. The air actuator provides a linear motion to the cylindrical Zirc-4 samples with an approximate velocity of 100 mm/s. In the heating zone, the sample was heated up to 700 °C externally by a 312 W tape heater with fast ramp rate (30 °C/min) and temperature was monitored by a K type thermocouple (1.6 mm in diameter) at the center of the sample. The measurement uncertainty was assumed to be ± 1.1 °C, as provided by manufacturer (Omega Engineering Corp). The chamber pressure was regulated by compressed argon gas, an inlet pressure regulator, and a back-pressure regulator. The pressure was maintained at 0.5 MPa with a fluctuation of 0.4×10^{-2} MPa during the pressurized experiment. A pressure transducer measured the system pressure with $\pm 1.0\%$ uncertainty. The Teflon seal assembly, containing three Teflon O-rings, allowed the linear motion of the sample and maintained the high pressure in the quenching chamber. Temperature of the water pool, filled by 1.4 L of deionized water, was also controlled by an external 624 W tape heater and bubble generation during quenching was visualized through borosilicate windows. A data acquisition system (National Instruments) with a sampling rate of 10 Hz was used to record the sample temperature, quenchant temperature, and chamber pressure during quenching experiments.

The first step for the experiment was boiling the deionized water in the quenchant pool for 20 min to remove any dissolved gas before controlling system conditions (e.g. increasing pressure or decreasing water temperature). When temperature of the sample reached 700 °C, the air actuator was activated to plunge the sample into the water pool. The transient boiling behavior was analyzed using the temperature history of the sample and the

bubble dynamics. Boiling curves (i.e. surface temperature vs. surface heat flux) were estimated by commercial inverse heat transfer software, INTEMP (Version 5.1., Nov. 2009) to determine the transition point in boiling regimes. The conventional uncertainty analysis for the ill-posed problem is difficult but detailed sensitivity analysis for the INTEMP model has been performed in a previous study [24], showing that the outputs appeared to be reliable. Furthermore, a minimal uncertainty of INTEMP calculations for surface temperature and heat flux during water quench experiment of cylindrical Zr samples was reported by Kang et al. [15]. In addition, surface roughness and static water contact angle for the quenched samples were measured by a white light

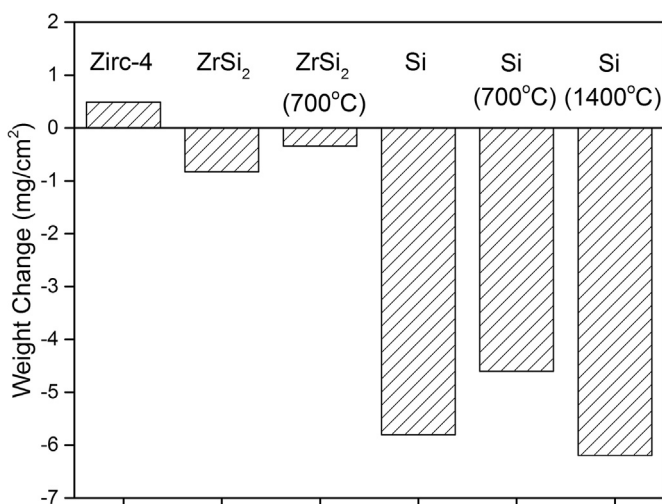


Fig. 3. Weight change of bare Zirc-4, ZrSi₂, Si, and pre-oxidized ZrSi₂ and Si (pre-oxidation conditions are 700 °C for 100 h and 1400 °C for 5 h in ambient air, respectively) after the corrosion test at 400 °C steam and 10.3 MPa for 72 h.

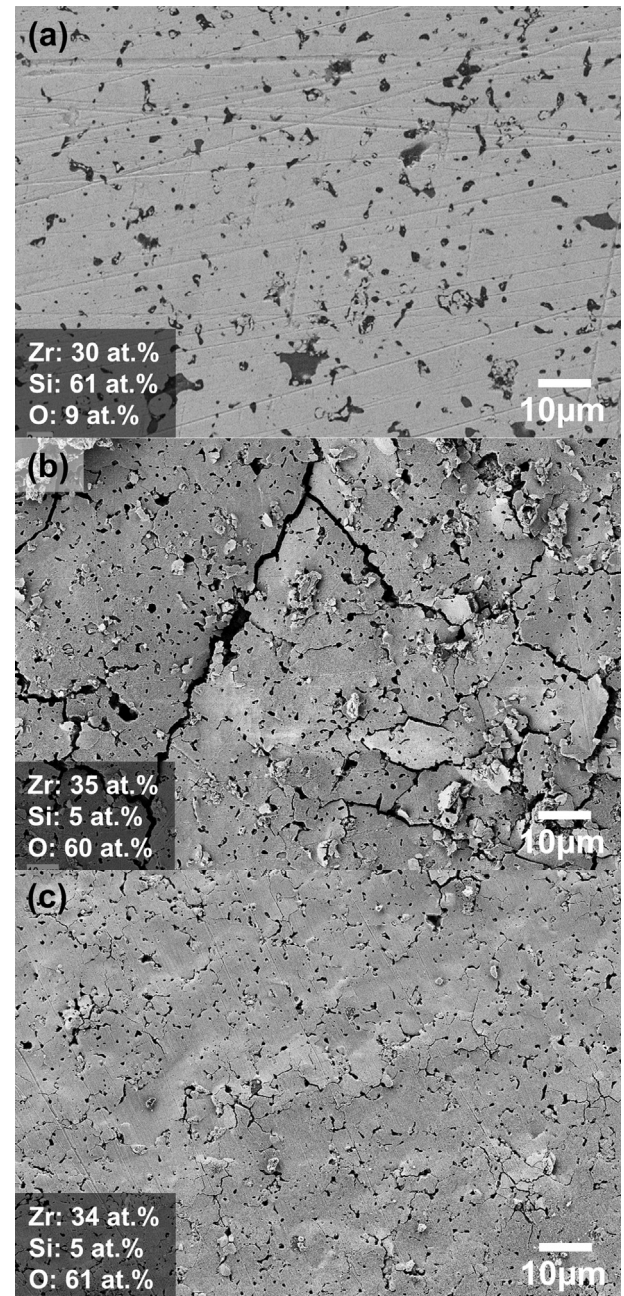


Fig. 4. Plan-view SEM images of (a) as-polished ZrSi₂, (b) ZrSi₂ after the steam test (ZrSi₂#1), and (c) pre-oxidized ZrSi₂ (700 °C air for 100 h) after the steam test (ZrSi₂#2). Composition of the surface (atomic percent) is stated on each figure, as measured by EDS surface scan analysis.

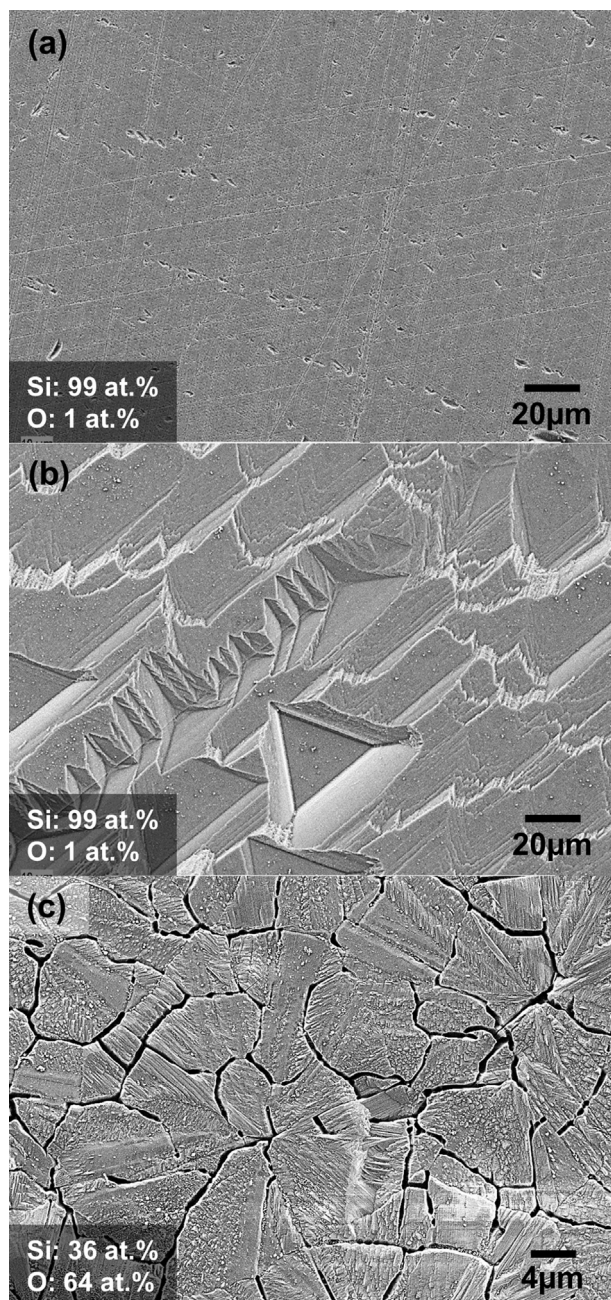


Fig. 5. SEM plan-view images of (a) bare Si, (b) the pre-oxidized Si (Si#2–700 °C air for 100 h), and (c) the pre-oxidized Si (Si#3–1400 °C air for 5 h). The samples were corroded under the steam condition. The silicon and oxygen atomic percentages on each surface are specified.

interferometry microscope (Zygo optical profilometer) and water contact angle measurement instrument (Dataphysics OCA 15), respectively. Table 1 summarizes sample compositions and experimental conditions in the study.

3. Results and discussion

3.1. Steam corrosion of bulk ZrSi_2 and bulk Si samples

Corrosion resistance of the bulk ZrSi_2 in pressurized steam condition was investigated by measuring weight changes in the samples and SEM-EDS characterization. Zirc-4 flats and single

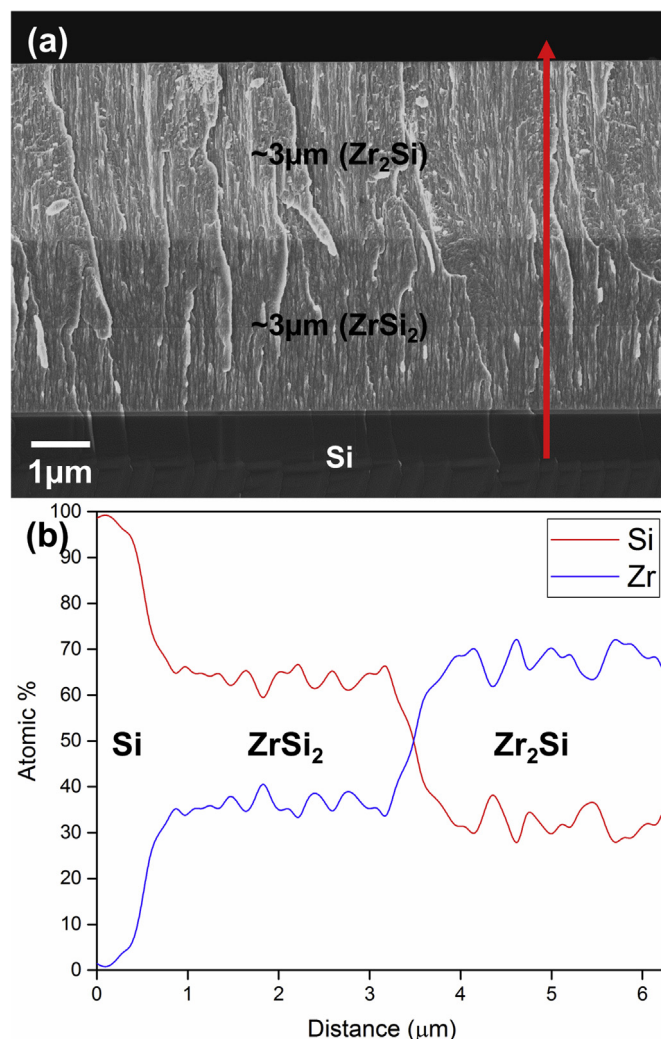


Fig. 6. (a) Cross-sectional SEM image of the multilayered coating (CZrSi#3) on Si wafer placed adjacent to the Zirc-4 samples during deposition and (b) EDS line scan percent of the compositional analysis of the coating, corresponding to the red arrow in (a). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

crystal silicon flats were introduced in the autoclave as reference samples. Some ZrSi_2 and the Si samples were pre-oxidized in at high temperatures (700 °C for 100 h or 1400 °C for 5 h, in ambient air) to demonstrate the effect of surface oxidation on corrosion behavior. The pre-oxidation processes resulted in thin oxide layers on the samples - the 700 °C oxidation for ZrSi_2 produced 1.3 μm oxide scale consisting of nanocrystalline ZrSiO_4 and quartz SiO_2 while pure Si samples formed 85 nm thick quartz SiO_2 layer. Cristobalite SiO_2 (1.5 μm in thickness) was formed on Si surface during the 1400 °C air oxidation.

The weight changes for the samples after the steam test are summarized in Fig. 3. All samples showed weight loss after the test except for the bare Zirc-4. The weight of the bare silicon and pre-oxidized silicon samples decreased significantly, suggesting that corrosion of Si in ZrSi_2 may also be a primary factor for the weight loss of ZrSi_2 samples. The weight loss was alleviated by the 700 °C oxidation for both ZrSi_2 (58%) and Si (20%) compared to the un-oxidized, as-received samples but explanation for this observation is not clear.

Plan-view SEM images for the bulk ZrSi_2 and the pre-oxidized ZrSi_2 at 700 °C air with compositional analysis after the steam

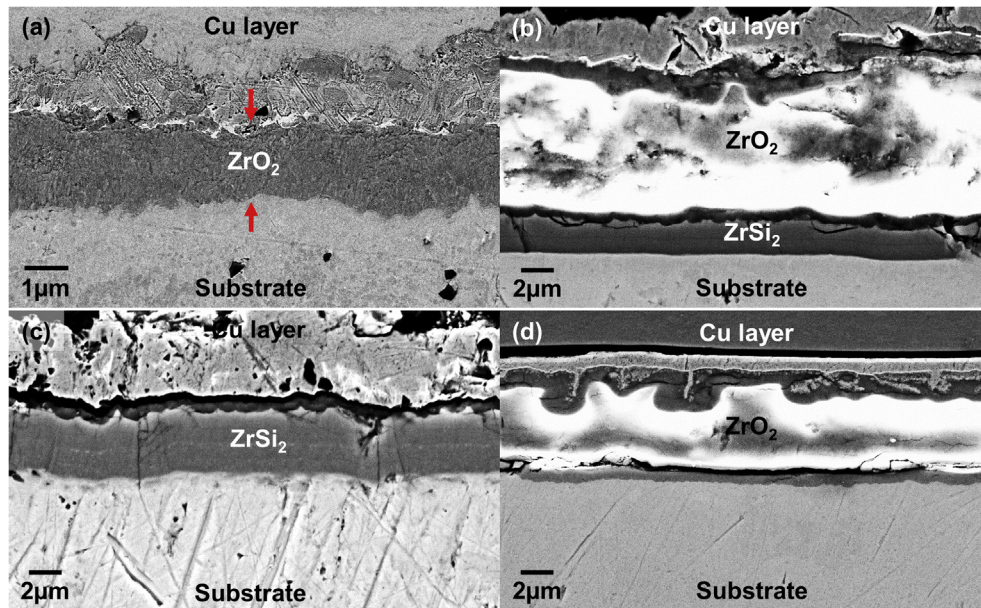


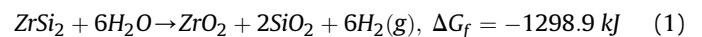
Fig. 7. Cross-sectional SEM images of (a) bare Zirc-4, (b) the ZrSi₂ coating (CZrSi#1), (c) ZrSi₂ pre-oxidized at 700 °C air (CZrSi#2), and (d) the pre-oxidized multilayered coating at 400 °C air (CZrSi#4). The samples were corroded under the steam condition. The Cu plating was deposited on the corrosion surfaces for surface protection during sample preparation. The arrows indicate the Zr-oxide scale.

autoclave test are shown in Fig. 4. The corroded ZrSi₂ (ZrSi₂#1) surface revealed surface cracks and pores. The silicon impurities in the ZrSi₂ matrix (Fig. 4a) may be leached out during the steam corrosion, resulting in pore formation. Mechanical integrity of the top surface was also poor as evidenced by number of debris particulates on the surface. On the other hand, the pre-oxidized surface (ZrSi₂#2) was smoother and cleaner than the bare ZrSi₂ surface. Although surface pores were observed in the image, severe cracks and local delamination of corroded layer were not identified. The observation is consistent with the result of the weight change (Fig. 3), which indicates that the pre-oxidation of ZrSi₂ mitigated the weight loss. However, nano-scale porous surface structures and significant reduction of silicon concentration on the top surfaces of both bare and the pre-oxidized ZrSi₂ were identified, supporting the hypothesis that the material degradations of ZrSi₂ was caused by a loss of silicon species in ZrSi₂.

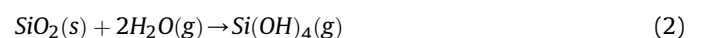
SEM imaging results of the silicon samples after the steam test were consistent with the weight loss. The high temperature steam reacted with the silicon samples which resulted in distinct surface morphologies as shown in Fig. 5. Before the steam test, all silicon samples were smooth and only polishing marks were identified (Fig. 5a). Oxygen concentration on the surfaces increased with increasing temperature of the pre-oxidation in ambient air. After the steam test, the surfaces became rough and noticeable surface texture was observed. The high temperature steam attacked preferential areas on the pre-oxidized Si surface at 700 °C air (Si#2), resulting in the microscale facets (Fig. 5b). Negligible oxygen concentration on the surface after the steam test indicates complete removal of the thin oxide layer. In addition, the network of micron cracks on local area of the pre-oxidized Si at 1400 °C air (Si#3) was revealed after the steam test as shown in Fig. 5c. The oxide scale was not fully consumed, but rather the grain boundaries of SiO₂ cristobalite grains were mainly corroded. It is speculated that the corrosion of grain boundary weakened mechanical integrity of the oxide scale and resulted in local spallation of the scale and associated with the large weight loss.

The loss of silicon in ZrSi₂ and in Si samples that occurred in the

steam environment was not observed in high temperature air [23]. An example of the effects of water vapor on oxidation in transition-metal silicides, using MoSi₂, was presented by Wood et al. [25]. The authors reported mass gain of MoSi₂ in atmospheric water vapor (75% steam and 25% Ar) at 600 °C was 100 times higher than that in dry air condition, and proposed that the water vapor inhibited formation of a passive SiO₂ layer followed by a formation of Mo oxide. The postulated reaction between ZrSi₂ and water vapor at 400 °C, calculated by HSC Chemistry thermodynamics software, is as follows:



The corrosion products should have a dense microstructure and good adhesion to the base material to act as a passive layer. However, the SiO₂ formed dissolves in by water to some extent. Fournier and Rowe [26] measured concentration of dissolved SiO₂ species in water during a high pressure autoclave test using colorimetric method. They reported that the solubility of amorphous SiO₂ in pure water increased exponentially with increasing water temperature and found a linear relationship between the solubility and autoclave pressure. Moreover, volatility of SiO₂ would also contribute to degradation of the surface oxide scale of ZrSi₂. Opilia et al. [27] concluded that volatilization of SiO₂ at high temperatures was dominated by the reaction (Eqn. (2)) with a linear kinetics. Moreover, surface recession of SiC was accelerated in a high-pressure steam environment (1200 °C and 2.07 MPa) due to enhanced volatility of SiO₂ in the pressurized condition.



Finally, at low oxygen partial pressures in water environment the formation of non-protective SiO rather than SiO₂ would occur, which could also lead to degradation of ZrSi₂. In short, the postulated reactions between silicon species and water vapor occurred and removed the silicon on ZrSi₂ surface, and the remaining zirconium species was oxidized and formed the non-protective porous ZrO₂ scale.

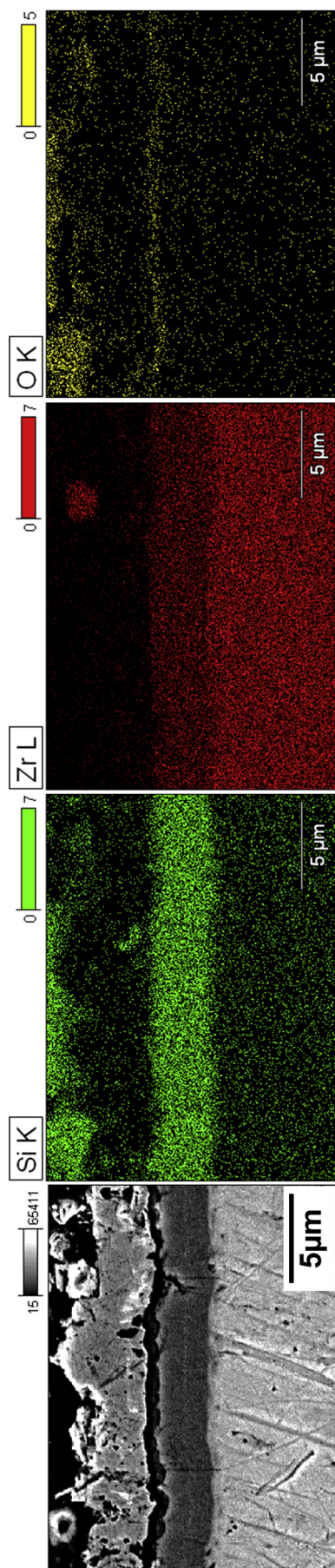


Fig. 8. SEM image and EDS elemental mapping of the pre-oxidized ZrSi_2 (CZrSi#2) after the steam test, showing the unreacted ZrSi_2 coating on Zirc-4 substrate.

3.2. Steam corrosion of zirconium-silicide coatings

Three zirconium-silicide coating concepts were investigated for steam corrosion: (i) ZrSi_2 coatings with thickness of $3.9 \mu\text{m}$ deposited on one surface of Zirc-4 (CZrSi#1), (ii) ZrSi_2 coatings deposited on Zirc-4 and pre-oxidized at 700°C air for 5 h prior to the steam test in order to attain a corrosion resistant layer (CZrSi#2), and (iii) a double-layered Zr-Si coating deposited on Zirc-4 substrate with the inner layer being ZrSi_2 with a thickness of $3 \mu\text{m}$ and the outer layer being Zr_2Si with thickness of $3 \mu\text{m}$ (CZrSi#3). As shown in Fig. 6a, the brighter area represents the Zr_2Si layer, containing more zirconium and less silicon. The EDS line scan confirmed composition of the coating system (Fig. 6b) and (iv) double-layered coatings oxidized at 400°C air for 10 h to promote formation of ZrO_2 on the top surface (CZrSi#4) (composition analysis on the oxidized coating showed an increase in oxygen concentration to 40 at.%).

Cross-sectional SEM analysis of the coated samples was performed after the autoclave test (Fig. 7). The oxide layer developed on bare Zirc-4 surface had an average thickness of $1.8 \mu\text{m}$, which is consistent with other experimental data for zirconium-alloys after corrosion tests under similar conditions [28,29]. All zirconium-silicide coatings reacted with steam, resulting in a thick and porous zirconium-oxide layer and in depletion of silicon. The oxide scale was so weak that it was easily damaged and removed during sample preparation for the SEM imaging. Therefore, the oxide layer is not seen in Fig. 7c. The images show that the ZrSi_2 coating (CZrSi#1, CZrSi#2) prevented oxide formation at the interface with the underlying Zr-4 alloy substrate. The pre-oxidized ZrSi_2 coating (CZrSi#2) had thicker unreacted ZrSi_2 coating than the as-deposited coating (CZrSi#1). The presence of unreacted ZrSi_2 coating in the pre-oxidized coating (CZrSi#2) was verified by EDS elemental mapping as shown in Fig. 8. A small portion of the coating ($\sim 1.1 \mu\text{m}$) was removed during the steam test but the rest of the coating was intact. The trend is consistent with the result of steam corrosion of bulk ZrSi_2 with the pre-oxidation treatment. The result indicates that the thin oxide layer formed at 700°C air is beneficial to mitigating a kinetics of the steam reaction. It is speculated that the oxide scale consisting of amorphous-nanocrystalline phases formed on the surface of ZrSi_2 in 700°C air [11] acts as a diffusion barrier even if SiO_2 species has a tendency to dissolve or volatilize in steam environment. However, the double-layered coatings (CZrSi#3, CZrSi#4) were fully oxidized so that a thin oxide scale was observed on the substrate. Table 2 provides a summary of corrosion performance of the zirconium-silicide coatings under the steam test. It is evident that the pre-oxidized ZrSi_2 coating (CZrSi#2) shows the best corrosion resistance compared to other tested coatings based on the minimal coating consumption.

3.3. Formation and steam corrosion of ZrSiO_4 surface layer

A ZrSi_2 coating, with a thickness of $3 \mu\text{m}$, was deposited on one surface of the SiC flats (CZrSi#5) and then oxidized at 1400°C for 5 h in ambient air. The high temperature oxidation of the ZrSi_2 coatings resulted in the formation of zircon (ZrSiO_4), a highly corrosion resistant material with potential to mitigate oxidation in extremely high temperature environments. Furthermore, the zircon structure may be expected to effectively immobilize silicon atoms and prevent silicon loss during exposure to water vapor environments. The SiC flats were chosen as substrates because Zirc-4 substrate could be excessively oxidized during the high temperature heat treatment due to oxygen ingress through uncoated area (the sputter deposition system is a light-of-sight process so a flat sample is generally not fully coated).

Table 2

Summary of corrosion of the zirconium-silicide coatings under 400 °C steam and 10.3 MPa for 72 h.

Sample ID	Composition, thickness, pre-oxidation condition	Remained coating (μm)	Substrate oxidation (μm)
Zirc-4	Zirc-4	N/A	1.8 ± 0.2
CZrSi#1	ZrSi ₂ , 3.9 μm	1.5 ± 0.1	None
CZrSi#2	ZrSi ₂ , 3.9 μm, 700 °C air 5 h	2.8 ± 0.1	None
CZrSi#3	Zr ₂ Si - ZrSi ₂ , 6 μm	Fully reacted	0.6 ± 0.1
CZrSi#4	Zr ₂ Si - ZrSi ₂ , 6 μm, 400 °C air 10 h	Fully reacted	0.6 ± 0.1

Fig. 9 shows cross-sectional microstructure and x-ray diffraction pattern of the oxidized ZrSi₂ coating (CZrSi#5). The oxide scale of the coating consisted of a continuous zircon layer with an average thickness of 1.9 μm, a SiO₂ layer, and islands of unreacted ZrSi₂. The thickness of the oxide scale was doubled (~5.4 μm) compared to the

as-deposited coating (~3 μm) due to increase in specific volume due to the formation of ZrSiO₄ and SiO₂. The composition and phases were determined based on compositional analysis by EDS point

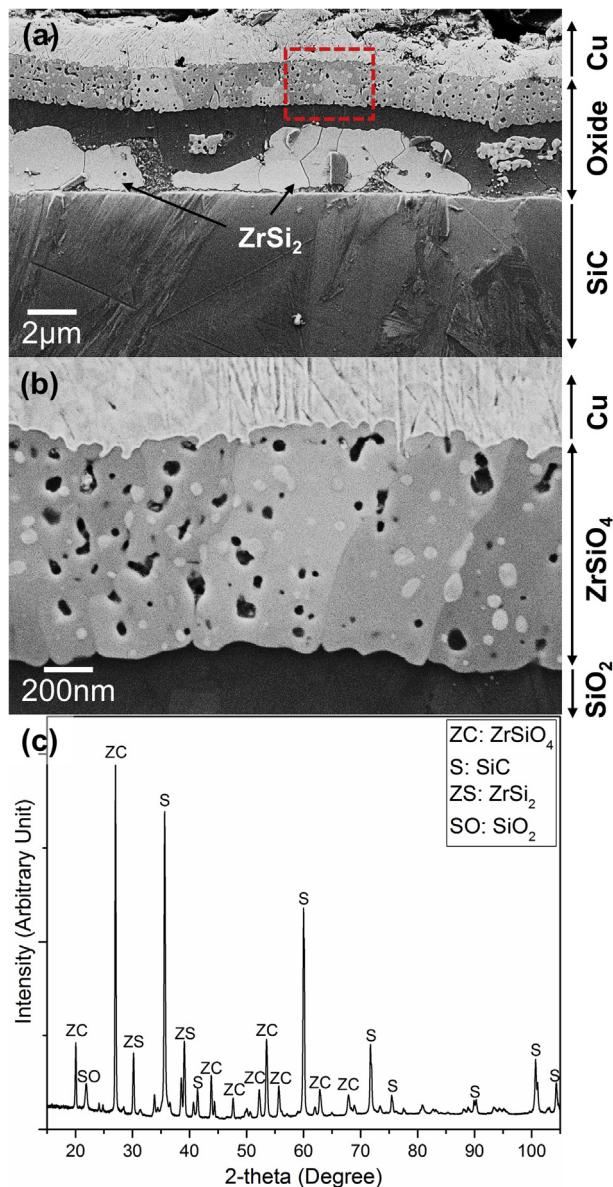


Fig. 9. Cross-sectional SEM images of oxidized ZrSi₂ coating (CZrSi#5) on the SiC substrate at (a) low and (b) high magnification, and (c) XRD pattern of the coating. Oxidation was performed at 1400 °C air for 5 h in ambient air. The high magnification image was acquired in the area indicated by the red frames in the low magnification image. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

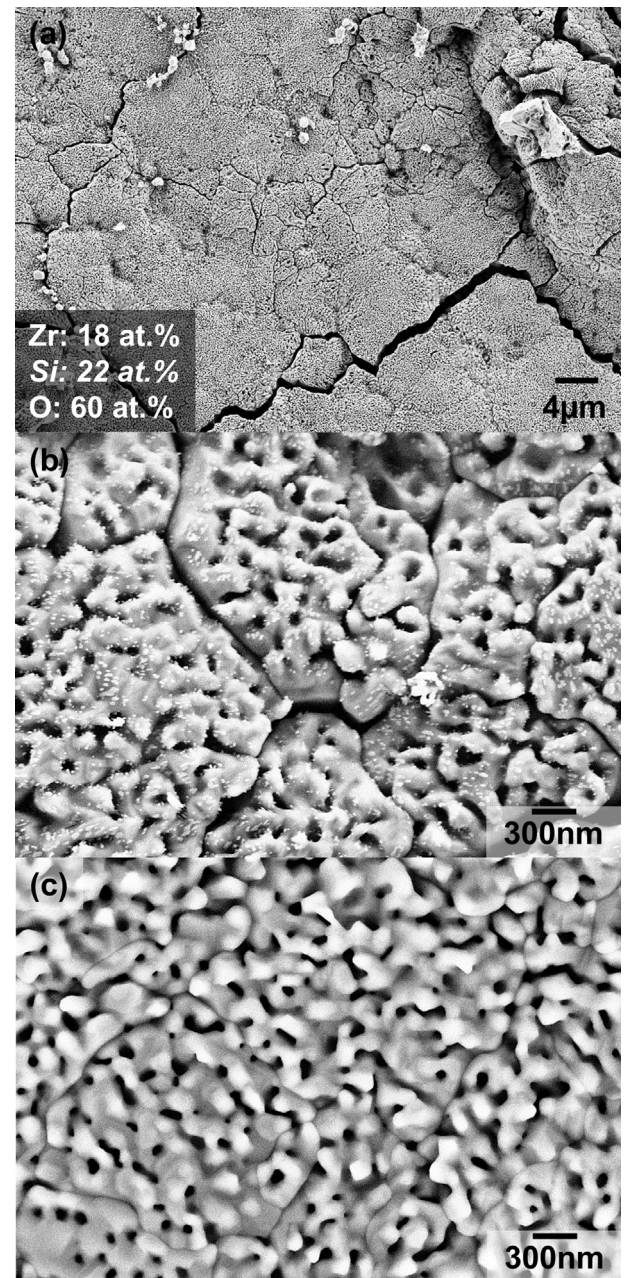


Fig. 10. Plan-view SEM images of the zircon formed ZrSi₂ coating (CZrSi#5) after the steam test at (a) low and (b) high magnification, and (c) the as-prepared zircon formed ZrSi₂ coating. Composition of the surface (atomic percent) is stated on each figure, as measured by EDS surface scan analysis.

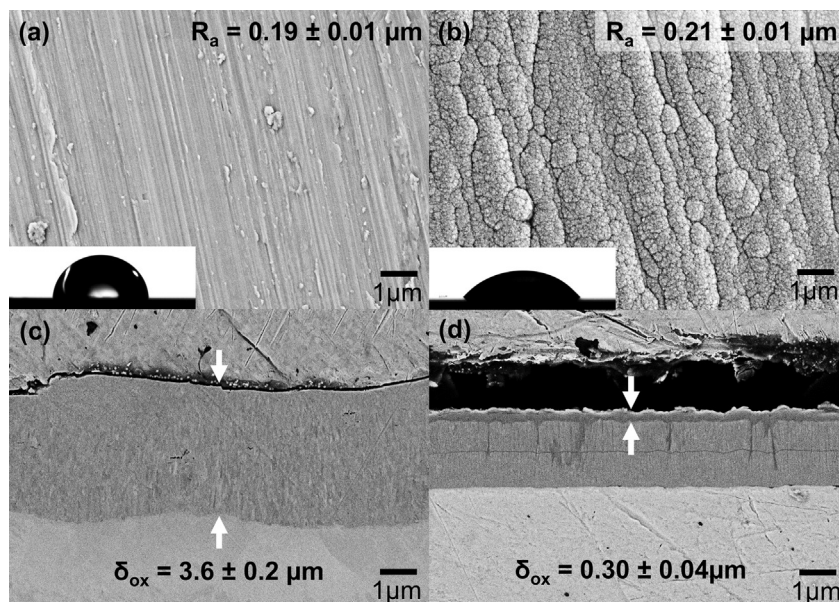


Fig. 11. SEM surface morphology characterized of (a) bare Zirc-4 surface and (b) ZrSi_2 coated Zirc-4 surface (CZrSi#6). (Inset) Photograph of a water droplet on each surface condition. Average surface roughness (R_a) for each condition is specified in the images. Cross-sectional SEM image of (c) the bare Zirc-4 and (d) the ZrSi_2 coated Zirc-4, showing thickness of the oxide layer and the coating. All samples were quenched for three times in atmospheric saturated water prior to the characterizations.

scans and the XRD pattern. The zircon layer has a columnar structure with a small volume fraction of nano-sized ZrO_2 and SiO_2 phases associated with the contrast difference in the high magnification image (Fig. 9b). It appears that the dark spots and the bright circles in the zircon layer are SiO_2 and ZrO_2 , respectively. Plausible mechanism of formation of the oxide scale is proposed using the oxidation data of bulk ZrSi_2 and ZrSi_2 coatings at 1000 °C and 1200 °C air [11,23]. The initial oxidation can be described that the top region of the ZrSi_2 coating reacts with oxygen, leading to precipitation and growth of ZrO_2 phase in SiO_2 matrix. Following this, solid state reaction of the ZrO_2 phases and the SiO_2 produces the ZrSiO_4 layer and the coalescence of the two phases proceeds as the reaction progresses [30]. Inward diffusion of excessive Si during the initial oxidation then results in the SiO_2 layer underneath the zircon scale. The excellent oxidation resistance of the zircon and SiO_2 scales mitigates oxidation kinetics, leading to the large unreacted ZrSi_2 coating zone underneath SiC substrate protected from oxidation. It is known that fabrication of zircon coating is a difficult process. For example, thermal spray of this material is limited due to phase decomposition during melting the feed powders above 1670 °C [31,32] and formation of micron-scale thickness of zircon layers takes very long time via atomic layer deposition.

Surface morphology of the zircon formed ZrSi_2 coating (CZrSi#5) after the steam autoclave test is presented in Fig. 10. The low magnification image (Fig. 10a) show cracks and partial delamination of the oxide scale. However, very importantly the EDS result for the surface shows that the elemental composition was not altered by the steam test. This indicates that silicon in zircon is greatly immobilized in steam environment and the zircon phase remained resistant to the corrosive environment. As a comparison of the high magnification images of as-prepared coating and the corroded coating (Fig. 10b and c), the grain boundaries of zircon phases were preferentially attacked by water vapor so that the surface etching was localized. The corrosion process led to water vapor infiltration through coating and its reaction with the underneath SiO_2 layer, weakening mechanical integrity of the zircon layer. Ueno et al. [33] reported the same phenomenon during static water corrosion test (1300 °C for 100 h) for bulk ZrSiO_4 samples.

The authors observed that amorphous SiO_2 -rich phases present at the grain boundaries of ZrSiO_4 compound, and hence easily corroded by water vapor. The present study demonstrated that forming a zircon layer is highly effective in immobilizing Si in normal LWR water environments, however compactness of the zircon grains must be improved (minimizing surface area of grain boundaries) to be a practical solution to the corrosion issue. Optimization of the zircon coating for greater compositional and morphological uniformity is currently in progress.

3.4. Water quenching of ZrSi_2 coatings

Quenching experiments of Zirc-4 tubes coated with ZrSi_2 of 2.1 μm in average thickness (CZrSi#6) were performed to examine an effect of the coating on water quenching performance and a robustness of the coating under thermal shock. Results of surface characterization for the bare sample and the ZrSi_2 coated sample after three repeated quench tests are shown in Fig. 11. The bare surface reveals minor scratches with directionality from the polishing process, and the coated surface shows the typical sputter coating morphology with a bulbous structure. Both surfaces were smooth so that average surface roughness (R_a) for the bare surfaces and the coated surfaces were $0.19 \pm 0.01 \mu\text{m}$ and $0.21 \pm 0.01 \mu\text{m}$, respectively. In addition, both surfaces were wettable - the static water droplet contact angle for the bare surfaces and the coatings were $86 \pm 3^\circ$ and $54 \pm 8^\circ$, respectively. Average oxide scale thickness of 3.6 μm was identified on the bare Zirc-4 samples after exposure to three sequential quenching treatments (Fig. 11c). It was found that the oxide scale was developed while the sample was heated up to 700 °C (initial temperature of quenching) and reacted with steam environment prior to plunging into the water pool. On the other hand, the ZrSi_2 coating mitigated the steam corrosion, leading to formation of submicron oxide layer (approximately 0.3 μm) on the top of the coating without any cracking, delamination, oxidation of the substrate. The absence of oxidation of the substrate is associated with the protective nature of the ZrSi_2 coating at 700 °C as observed in the ZrSi_2 coatings (CZrSi#2) in the steam test, and silicon depletion in the coating was not clearly identified in the experiment.

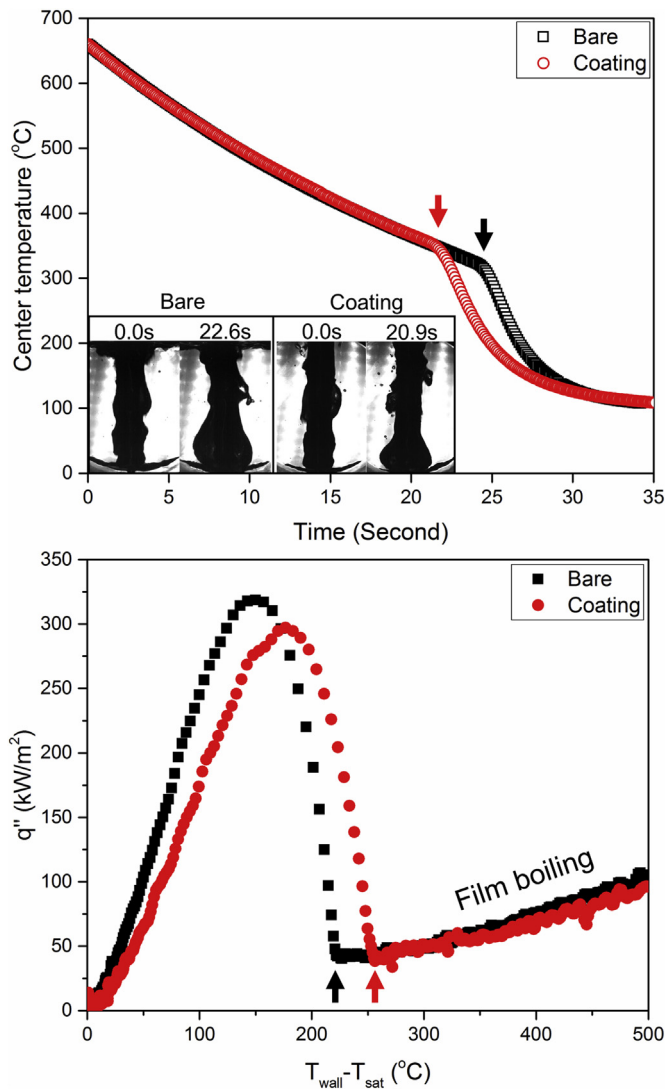


Fig. 12. (a) Quenching curves, (inset) a snapshot of film dynamics for the bare and coated samples, and (b) boiling curves of the bare sample and the ZrSi₂ coated Zirc-4 samples in atmospheric saturated water. The minimum film boiling points are indicated by the arrows.

Quenching performance of the bare Zirc-4 sample and the ZrSi₂ coated sample in atmospheric saturated water was analyzed using the quenching curves (temperature vs. time), the boiling curves (surface heat flux vs. surface superheat), and the high-speed images as shown in Fig. 12. The center temperature of the both samples decreases gradually as the cooling progresses. This corresponds to the film boiling regime where vapor film fully covers the hot surface while pulsating in oscillatory motion as shown in the high-speed images right after quenching (0.0s) in Fig. 12a. The inflection points for the coating in the quenching curve (Fig. 12a) occurred earlier in time during the quench process than the bare sample, which is also confirmed in the high-speed images that the coated sample showed earlier destabilization of vapor film at the bottom of the sample (20.9 s) compared to the bare sample (22.6 s). Furthermore, the boiling curves (Fig. 12b) show that film boiling heat transfer for both surfaces were well matched but the minimum film boiling temperature – closely related to the inflection point in the quenching curve, a lower limit of film boiling regime, for the coating was approximately 20 °C higher than that of the

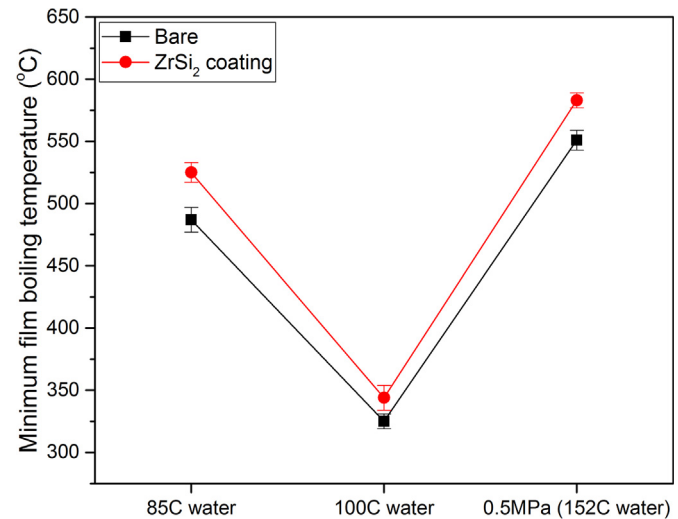


Fig. 13. Average minimum film boiling temperature for the bare samples and the ZrSi₂ coated Zirc-4 samples in the three experimental conditions – atmospheric subcooled water (85 °C water), atmospheric saturated water (100 °C water), and saturated water at 0.5 MPa (152 °C water). The test was performed at least three times in each condition to ensure statistically significant results.

bare surface. From a practical standpoint, it is important for fuel cladding surface to have a higher minimum film boiling temperature during quenching. This is because a heat removal from the heated surface in the film boiling regime is quite limited. The results suggest that the ZrSi₂ surface coating is beneficial to enhance quenching performance to some extent in saturated water at atmospheric pressure.

Fig. 13 summarizes the minimum film boiling temperatures of the ZrSi₂ coated samples at atmospheric saturated water, saturated water (152 °C) at 0.5 MPa, and atmospheric subcooled water (85 °C). The cooling behavior was significantly affected by the environmental conditions and the minimum film boiling point was increased by 6–8% with the ZrSi₂ coating regardless of the environmental conditions.

The increase in minimum film boiling temperature by the ZrSi₂ coatings could be explained by thermal properties of the coating. Other surface conditions (i.e. wettability and surface roughness – please see Fig. 11a and b) were similar in both bare surfaces and coated surfaces. It was proposed that thermal properties of wettable surface were dominant factors in controlling quenching heat transfer [24,34]. It was hypothesized that liquid contacts on heated surface can remove a large amount of heat during quenching, leading to a significant temperature drop in localized areas. If a surface has a small thermal conductivity, the localized temperature drop cannot be readily recovered by lateral heat conduction, resulting in the acceleration of collapse of stable film boiling. Therefore, the ZrSi₂ coating is assumed to have a smaller thermal conductivity than Zirc-4.

Previous literature suggests that sputtered coatings have lower thermal conductivities than their bulk counterparts. For example, Cahill and Allen [35] showed that the thermal conductivity of a sputtered SiO₂ film deposited at 100 °C was 77% that of the bulk material even though the film had the same density as the bulk. Also, sputtered TiO₂ film at 250 °C had the thermal conductivity approximately 66% that of the bulk material, but the conductivity of a film deposited at higher temperature (400 °C) approached bulk crystalline TiO₂ [36]. The study suggested that the thermal conductivity of sputtered coating is related to film density, grain size, and concentration of atomic-scale defects (interstitials or

vacancies), which were strongly dependent on the temperature of sputter deposition process. Since the ZrSi_2 coating was deposited at the low temperature (19 °C), it is plausible that thermal conductivity of the coating is much less than the reported value for bulk ZrSi_2 ($k = 15.6 \text{ W/m}\cdot\text{K}$ [37]). Furthermore, the ZrSi_2 coating was deposited by the multiple steps to achieve the desired thickness which may cause significant thermal resistance between each thin layer. Overall, the lower thermal conductivity of the ZrSi_2 coating was attributable to the higher minimum film boiling temperature correlating with an enhanced cooling ability during accident scenarios.

4. Conclusions

This study describes the results of steam corrosion tests of bulk ZrSi_2 and bulk Si as well as sputtered coatings of zirconium-silicide on Zircaloy-4 and SiC flats with compositional modulation and pre-oxidation treatments. In addition, water quenching behavior of ZrSi_2 coating on cylindrical Zircaloy-4 samples was performed to examine a feasibility of the coatings as a potential ATF cladding coating material in light water reactor. Steam corrosion testing (400 °C steam and 10.3 MPa for 72 h) led to weight loss of ZrSi_2 and resulted in a zirconium-oxide scale with silicon depletion, attributed possibly to volatile silicon hydroxide, gaseous silicon monoxide, and a solubility of silicon dioxide in water. Significant surface recession of Si samples after the steam test supported this hypothesis.

The zirconium-silicide coating ($\sim 3.9 \mu\text{m}$) with pre-oxidation at 700 °C air for 5 h was found to be the best condition to prevent oxide formation in zircaloy-4 substrate without spallation and cracking of the coating in the steam environment even if the top surface of the coating was degraded by formation of non-protective zirconium-rich oxide layer. Only the zircon phase (ZrSiO_4), formed by exposing the ZrSi_2 coating on SiC substrates at 1400 °C in air, allowed for immobilization of silicon species in the oxide scale in the steam environments.

Water quenching experiments of cylindrical Zircaloy-4 samples with average thickness of ZrSi_2 coating in $2.1 \mu\text{m}$ were performed in the different environmental conditions (the pressurized water or the subcooled water). Quenching heat transfer was improved by the surface coating; the minimum film boiling temperatures were increased in the range of 6–8% in these conditions possibly due to a small thermal conductivity of the ZrSi_2 coating. While these improvement factors are quite low, the study points to the potential use of coatings to beneficially affect heat transfer of the cladding. Even after three aggressive thermal cycles (e.g., water quenching from 700 °C to 85 °C in 20 s), the coating did not exhibit any surface degradation such as cracking or spallation.

The research results provided pathways for future research areas, including silicon depletion in zirconium-silicide in aqueous conditions, improvement uniformity of ZrSiO_4 layer produced by the high temperature oxidation, and use of coatings to improve heat transfer characteristics of the cladding.

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Transient pool boiling heat transfer of oxidized and roughened Zircaloy-4 surfaces during water quenching

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Surface roughness

ABSTRACT

The sensitivity of surface oxidation and surface roughness to transient pool boiling heat transfer was investigated by performing water quenching experiments of Zircaloy-4 rodlets under increased pressure or subcooled water. The results demonstrated that quenching behavior was notably affected by the surface oxidation and the surface roughness regardless of environmental conditions (saturated water at 0.5 MPa or $\Delta T_{\text{sub}} = 15$ K). The minimum film boiling temperature increased with the thickness of surface oxide (3.6 ± 0.2 to 55.6 ± 2.2 μm). Rough surfaces ($R_a = 11.4 \pm 2.5$ μm) showed a large surface heat flux with vigorous vapor generation even in the early stages of quenching. To explain the augmented quenching heat transfer by the surface modifications, a hypothesis that incorporates instantaneous heat transfer during liquid–solid contacts in the stable film boiling regime was proposed. The theoretical model with assumptions elucidated the bubble dynamics of the modified surfaces qualitatively and predicted minimum film boiling points depending on the degree of surface oxidation, which were in good agreement with experimental results. Both surface properties and parameters affecting liquid–solid contact are dominant factors in determining transient pool boiling heat transfer during water quenching.

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1. Introduction

Transient boiling phenomena during rapid quenching process has been important subjects for the chemical process industry, the steel-making industry, and nuclear power plants. Particularly, during loss-of-coolant accident scenario in light water nuclear reactors, transition from film boiling to nucleate boiling regime is desired as cold liquid refloods the overheated nuclear reactor core. As the fuel rods are rapidly immersed in cold water, the surface temperatures would be high enough to produce a vapor blanket with a low heat transfer rate. If the boiling mode changes from the film boiling to transition boiling, continuous wetting of the surface begins and the stable vapor blanket starts collapsing followed by vigorous nucleation of bubbles. Since the nucleation boiling regime has a higher heat transfer coefficient, the fuel claddings could be effectively cooled to equilibrium conditions. Therefore, accelerated cooling to the boiling transition point (i.e., increase in minimum film boiling temperature) is beneficial as it would mitigate further degradation of the fuel cladding and accurate prediction of the temperature is required for a design of safety system in light water nuclear reactors.

Suppose an accident scenario where a certain level of pressure is sustained in a reactor vessel and into which subcooled auxiliary water is injected and interacts with the fuel cladding rods. Here, the hot surface experiences the quenching process at pressurized conditions and the boiling heat transfer mechanisms may be different from those at atmospheric pressure. For example, theoretical models [1,2] based on Taylor instability and transient liquid contacts in film boiling regime predicted that T_{min} would increase with increasing system pressure due to changes in the thermal properties of the liquid and vapor. At elevated pressures (up to 1.1 MPa), earlier transitions of boiling regimes were observed for horizontal stainless steel and gold coated copper surfaces in saturated ethanol and water [3]. Additionally, it is known that liquid subcooling accelerates quenching due to an increasing contribution of sensible heat to surface heat removal and decrease in thickness of the vapor layer during stable film boiling. Experimental data shows that the minimum film boiling temperature (T_{min}) is linearly proportional to a degree of water subcooling in atmospheric pressure [4,5].

Transient boiling heat transfer is also affected by characteristics of the heated surface such as thermal properties, surface roughness, and wettability. Possible underlying mechanisms for enhancement of quenching heat transfer by surface modifications were introduced in the past literature. First, past research proposed that surface feature/roughness would promote a breakup of stable

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Nomenclature

Bi	Biot number
C_p	specific heat ($\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$)
D	diameter of liquid-contact area (μm)
fps	frames per second
k	thermal conductivity ($\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$)
P	pressure (MPa)
q''	heat flux ($\text{kW}\cdot\text{m}^{-2}$)
R	radius of liquid–solid contact (μm)
r	radial coordinate
R_a	arithmetic mean roughness (μm)
$T_{\min}$	minimum film boiling temperature ($^{\circ}\text{C}$)
T_{hm}	homogenous nucleation temperature of water ($^{\circ}\text{C}$)
ΔT_{sub}	water subcooling ($T_{\text{sat}} - T_{\text{water}}$) (K)
ΔT_{sup}	surface superheat ($T_{\text{surface}} - T_{\text{sat}}$) (K)
t	time (s)
x	axial coordinate

Greek letters

α	thermal diffusivity (m^2/s)
δ_{ox}	thickness of oxide scale (μm)
η	dummy variable
θ	static contact angle of water droplet ($^{\circ}$)
λ	dummy variable
ρ	density ($\text{kg}\cdot\text{m}^{-3}$)
τ	duration (ms)

Subscripts

ini	initial
local	local area
ox	oxide
sat	saturation temperature
surf	surface
w	water
z	zirconium

film boiling [6–11]. Surface features may penetrate a vapor layer covering a hot surface and contact the liquid, leading to disruption of the stable film boiling. Bradfield [11] postulated that liquid–solid contacts existed in the stable film boiling regime, and the contacts are periodic on smooth surfaces but it could be quasi-continuous if sufficient surface roughness existed. Second, it was suggested that enhanced hydrophilicity of nano/micro structures increased $T_{\min}$ in saturated or subcooled water. For example, the modified surfaces were prepared by repeated quenching of heated metals in nanofluid [12–14], a vapor deposition method [15], and anodic oxidation [16]. Finally, thermally insulated surface coatings (low thermal conductivity) showed high minimum film boiling temperatures under liquid nitrogen [17]. However, to the best of the authors' knowledge, little has been reported concerning the quenching phenomena for zirconium alloys with surface oxidation or roughness modifications. Furthermore, it is worth investigating if alterations in quenching behavior by these surface modifications at atmospheric pressure are sustained at different system conditions such as elevated pressures or subcooled water.

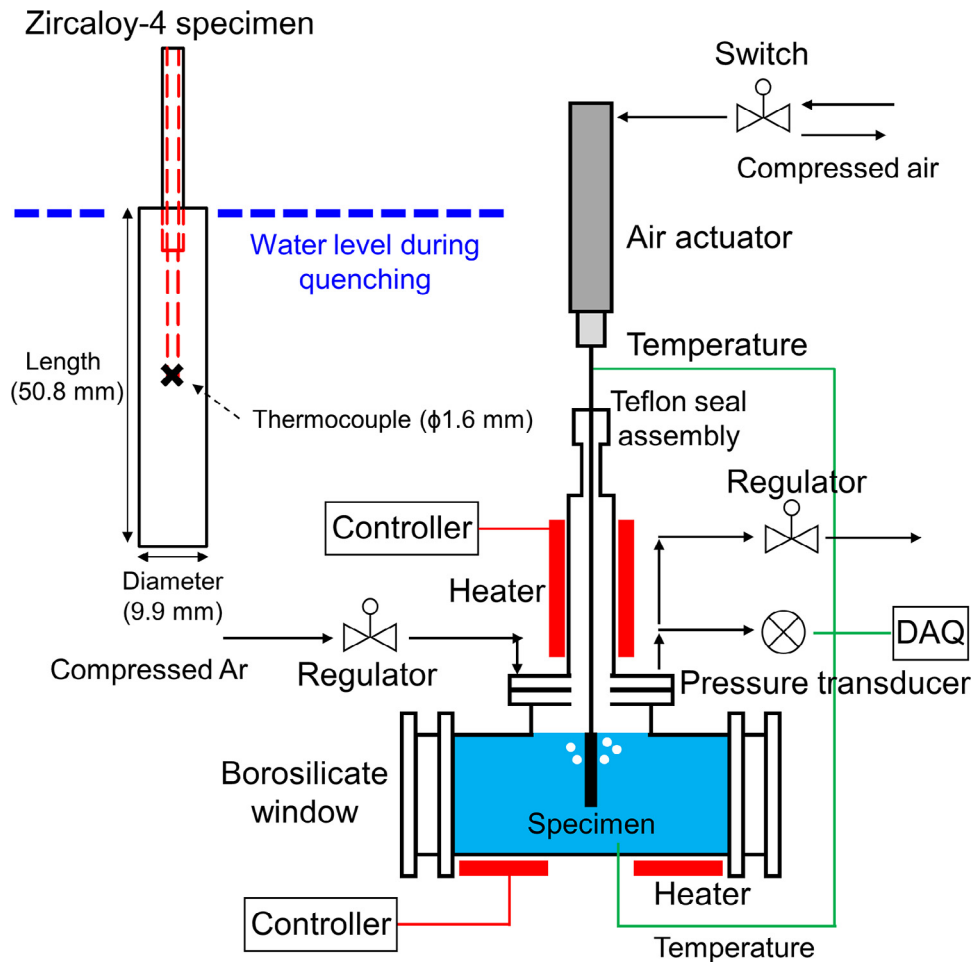
In this study, quench experiments using cylindrical Zircaloy-4 (Zirc-4) test sections were performed in a deionized water pool. Effects of surface oxidation and surface roughness of the Zirc-4 on transient heat transfer were investigated at three system conditions: (1) atmospheric saturated water, (2) saturated water at 0.5 MPa, and (3) 15 K subcooled water at atmospheric pressure. A hypothetical model based on instantaneous heat transfer during an intermittent liquid–solid contact is proposed to explain the experimental results regarding surface conditions on quenching behavior in the atmospheric saturated conditions. Temperature history at the center of each cylindrical sample was measured by a data acquisition system and bubble evolution was photographed using a high-speed camera during the quenching process.

2. Experiments

2.1. Experimental facility

A schematic diagram of the quenching test facility is shown in Fig. 1. The facility consisted of an air actuator, Teflon seal assembly, heating zone, cylindrical test section, and water quenching chamber. The air actuator (51 cm bore diameter and 30 cm stroke

length) was aligned concentrically with the top flange of the water chamber and provides a linear motion (approximately 100 mm/s) for the cylindrical test sample. The Teflon seal assembly included Teflon O-rings to maintain pressure in the quenching chamber during experiments while allowing a connecting tube for the sample to slip through in the linear motion. The sample could be heated to 700 $^{\circ}\text{C}$ externally in the heating zone by a 312 W heating tape covering the entire surface of the stainless housing tube. Zirc-4 rodlets were procured and machined to have 9.9 mm diameters and 51 mm lengths. A hole, stepped from 3.2 mm to 1.6 mm in diameter, was drilled from the top surface of each sample to install a K-type, ungrounded thermocouple (1.6 mm in diameter) with an Inconel sheath. It was tightly inserted via an interference fitting into the center of the sample. This thermocouple was chosen to minimize noise signal arising from thermal shock, the mechanical fitting, and electrical damage even if its response time (~ 0.25 s) might not be fast enough to record entire temperature transient during quenching. The present study utilized the same type of thermocouples to all experiments so that the experimental data are meaningful to understand the surface effects and system effects. Also, uncertainty of the temperature measurements was assumed to be ± 1.1 $^{\circ}\text{C}$, as provided by the thermocouple manufacturer (Omega Engineering Corp). The quenching chamber was a stainless steel butt-welded tee pipe which was welded to a weld-neck flange on each opening. A borosilicate window was placed on each end for visualization of bubble evolution. The quenching chamber could contain approximately 1.7 L of deionized water (18 M Ω -cm). The quenchant temperature was controlled by a 624 W heating tape installed on the outer surface of the quenchant chamber. The chamber pressure could be regulated by compressed argon gas, an inlet pressure regulator, and a back-pressure regulator. The desired pressure was set by the inlet pressure regulator and overpressure during the test was alleviated by the back-pressure regulator. A fluctuation of the system pressure at 0.5 MPa was 0.4×10^{-2} MPa. A pressure transducer and a mechanical pressure gauge were mounted on the top flange, monitoring the system's pressure. Measurement uncertainty of the pressure transducer was stated as $\pm 1.0\%$ (relative error) by the manufacturer (Omega Engineering Corp). A data acquisition system (National Instruments) with a sampling rate of 10 Hz, which is faster than the response time of the thermocouples, was used to record sample temperature, quenchant temperature, and chamber pressure. In addition, a high-speed camera (Motion Pro HS-3, capable of



The bare surface was prepared by polishing the as-machined surface with abrasive SiC polishing papers up to 600 grit. The surfaces with a thick oxide layer were prepared by performing pre-oxidation of the bare samples at 700 °C in ambient air with a 5 °C/min heating rate. The roughened surfaces were produced by dry sand blasting with alumina grit, resulting in micron-scale

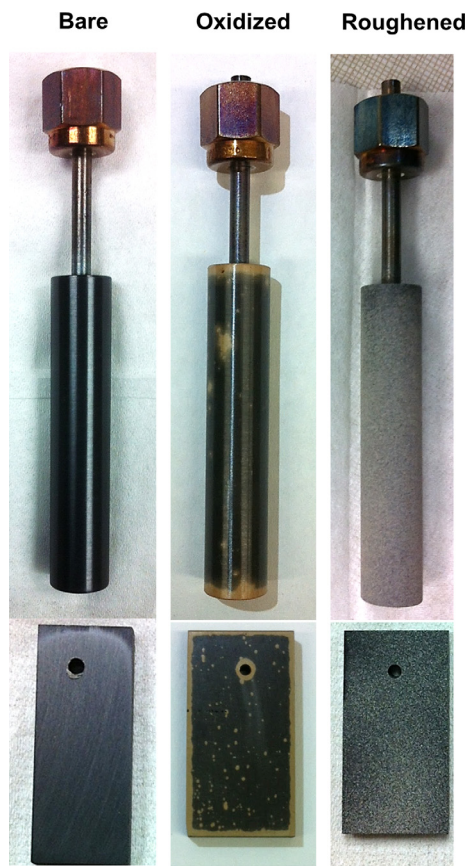


Fig. 2. Images of modified surfaces (bare surfaces, pre-oxidized surfaces at 700 °C air for 300 min, and roughened surfaces) on cylindrical and flat samples after three repeated quenching tests.

roughened surfaces. After the roughening process, the sample was sonicated for 20 min in an acetone bath to remove surface contaminants. In Fig. 2, photographs of the modified surfaces (Zirc-4 flats and Zirc-4 rodlets) after three repeated quenching tests are displayed. Originally, all surfaces were reflective metallic gray except for the pre-oxidized surfaces. After the quenching tests, both the bare and roughened samples showed color changes and less reflective surfaces, indicating the surfaces were oxidized. Table 1 summarizes the sample preparations and experimental conditions of the quenching tests.

2.4. Surface characterizations

The modified surfaces after three repeated quenching tests were characterized via SEM imaging (Zeiss LEO Scanning Electron Microscope), white light interferometry microscope (Zygo optical profilometer), and water static contact angle measurement (Data-physics OCA 15). The results of these studies are shown in Fig. 3.

The bare surface (Fig. 3a) and pre-oxidized surface (OX#3) (Fig. 3b) revealed smooth surfaces without any surface irregularities. Only fine scratches on the surface due to the polishing process were identified. The rough surfaces revealed micro-mechanical roughened morphology because the high kinetic energy of the alumina particles caused erosion of the surface. The water contact angle measurements showed that all the surface conditions exhibited hydrophilicity (contact angle $< 90^\circ$). For the bare surfaces, the contact angle was $\theta = 86 \pm 3^\circ$ and for the pre-oxidized surfaces (OX#3) it was $\theta = 65 \pm 5^\circ$. The roughened surfaces showed a contact angle of $\theta = 38 \pm 4^\circ$. The result showed that the pre-oxidized surfaces and the rough surfaces are more wettable than the bare surfaces but the decrease in water contact angle was not significant enough to cause any changes in quenching performance.

In addition, surface roughness (R_a) was measured for the bare surfaces and the pre-oxidized surfaces using the white light interferometry microscope, and the surfaces were smooth. R_a values for the bare surfaces and OX#3 surfaces were found to be approximately $0.21 \pm 0.02 \mu\text{m}$ and $0.26 \pm 0.03 \mu\text{m}$, respectively. The polishing scratches induced the surface roughness. Due to limited light reflection on the rough surfaces, the surface roughness was directly measured by image-processing of cross-sectional SEM images. As displayed in Fig. 3d, the rough surfaces had an average roughness (R_a) of $11.4 \pm 2.5 \mu\text{m}$. These roughness values are more than 50 times greater than those of the smooth surfaces. The local maximum height (distance from a peak to a valley) of structures on the rough surfaces was about $40 \mu\text{m}$, which is an order of magnitude smaller than the estimated vapor film thickness for vertical bare surface during film boiling in atmospheric, saturated water [18]. Kang et al. [6] proposed that continuous liquid–solid contact is thermodynamically available on microstructured surfaces due to a fin effect even at high wall superheats. However, thermal analysis for the postulated ZrO_2 surface features (a triangular solid fin had $45 \mu\text{m}$ of height and $20 \mu\text{m}$ of diameter) showed that the temperature drop due to the fin effect was too small to cause collapse of the stable film boiling [19]. Therefore, the surface roughness may not influence vapor film dynamics during the quenching process.

Cross-sectional SEM images were used for measuring the oxide layer thickness as shown in Fig. 4. During three repeated quenching tests, a thin zirconium oxide layer was grown on the bare surfaces, and the thickness was found to be approximately $3.6 \pm 0.2 \mu\text{m}$. The pre-oxidations followed by the tests produced a thick oxide layer of $8.8 \pm 0.1 \mu\text{m}$, $24.7 \pm 3.4 \mu\text{m}$, and $55.6 \pm 2.2 \mu\text{m}$ in thickness for OX#1, OX#2, and OX#3, respectively.

2.5. Determination of surface temperature and surface heat flux

The temperature history was measured by a thermocouple installed at the center of the cylindrical specimen during the quenching experiments. However, if spatial temperature distribution in the specimen cannot be neglected due to high Biot number of the modified surfaces, then surface temperature is a better indicator of thermal phenomena for the solid surface instead of the center temperature. In addition, determination of surface heat flux

Table 1

Summary of surface treatments for Zirc-4 samples and experimental conditions for quenching tests. Reference, pressurized, and subcooled in the table stand for quenching tests in saturated water at atmospheric pressure, in saturated water at 0.5 MPa, and in 15 K subcooled water at atmospheric pressure, respectively.

Sample ID	Surface treatment	Quenching test condition
Bare	Polishing by 600 grit abrasive paper	Reference, pressurized, subcooled
OX#1	Pre-oxidation at 700 °C air for 30 min	Reference
OX#2	Pre-oxidation at 700 °C air for 120 min	Reference
OX#3	Pre-oxidation at 700 °C air for 300 min	Reference, pressurized, subcooled
Rough	Alumina grit blasting	Reference, pressurized, subcooled

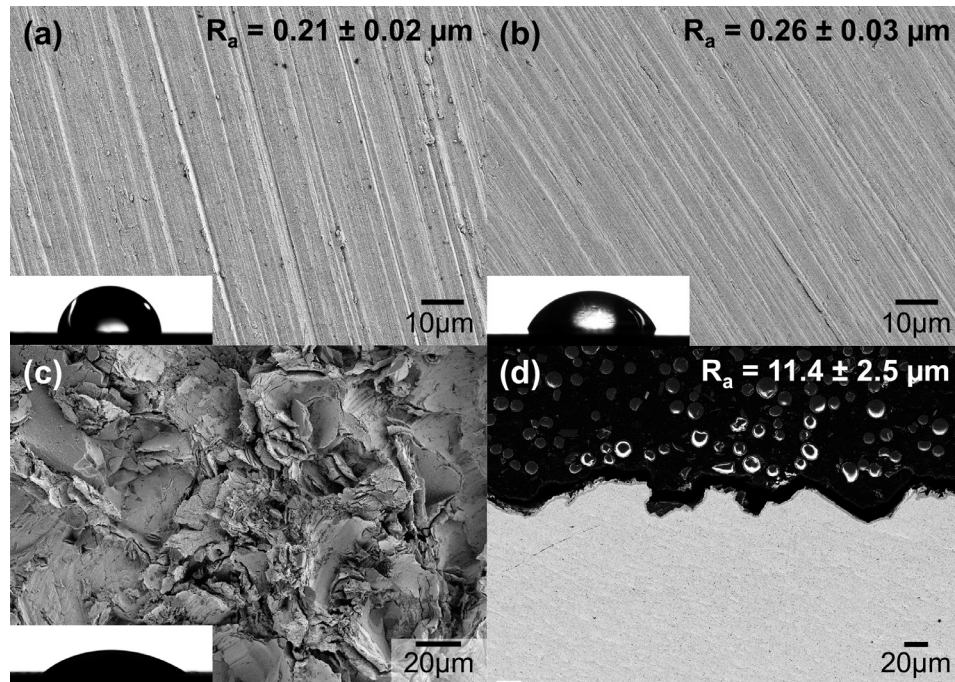


Fig. 3. Microscopic surface morphology characterized by SEM on (a) the bare surface, (b) the pre-oxidized surface (OX#3), and (c) the rough surface. (Inset) Photograph of a water droplet on each surface condition. (d) Cross-sectional SEM image of the rough surface. Average surface roughness for each condition is specified in the images. The samples were quenched for three times in saturated water at atmospheric pressure. Characterizations of pristine samples are not reported because all samples were eventually oxidized during the heating profile prior to the first quenching.

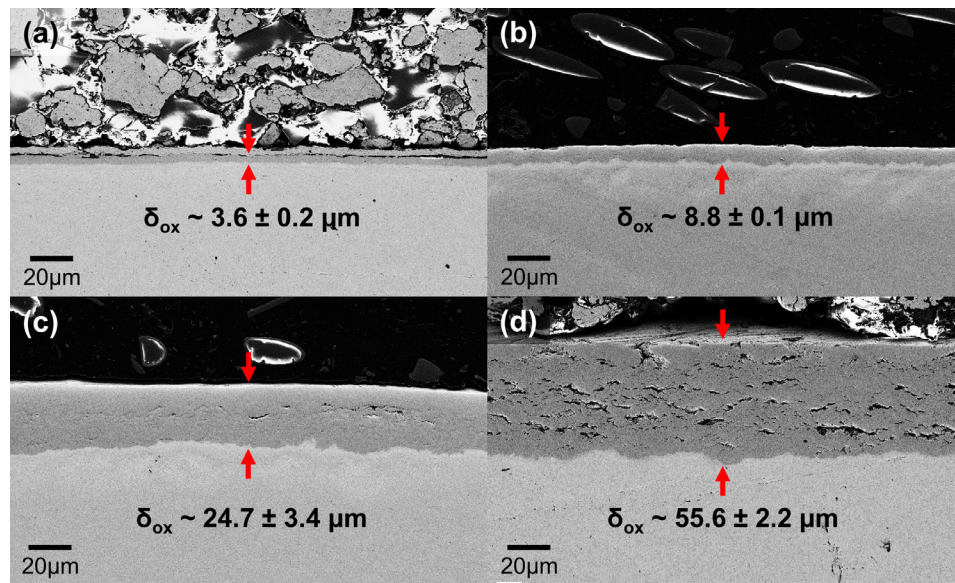


Fig. 4. Cross-sectional SEM images of oxidized samples after three quenching tests in saturated water at atmospheric pressure: (a) bare surface, (b) pre-oxidized at 700 °C air for 30 min (OX#1), (c) pre-oxidized at 700 °C air for 120 min (OX#2), and (d) pre-oxidized at 700 °C air for 300 min (OX#3). The oxide scale is indicated by the red arrows. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

was necessary to plot boiling curves, surface heat flux vs. surface superheat (ΔT_{sup}), which was used to evaluate the minimum film boiling temperature (T_{min}).

To obtain surface temperature and surface heat flux, an inverse heat transfer problem was solved by using INTEMP (Version 5.1, November 2009), a commercial inverse heat transfer software. The software is based on dynamic programming and finite element method [20,21]. The basic principle is to perform iterations, which compare both the measured temperature and estimated one based

on assumed boundary conditions (i.e., surface temperature and surface heat flux) until their difference falls below a predetermined threshold. The finite element model for a quadrant of the cylindrical test section in the present study is illustrated in Fig. 5, consisting of 561 nodes and 500 axisymmetric elements with temperature-dependent properties (i.e., ρ , k , and C_p) of Zircaloy (see Table 2). Since temperature–time data was available at a single location (the left bottom corner in Fig. 5), the boundary condition for the top surface was assumed to be a constant heat transfer

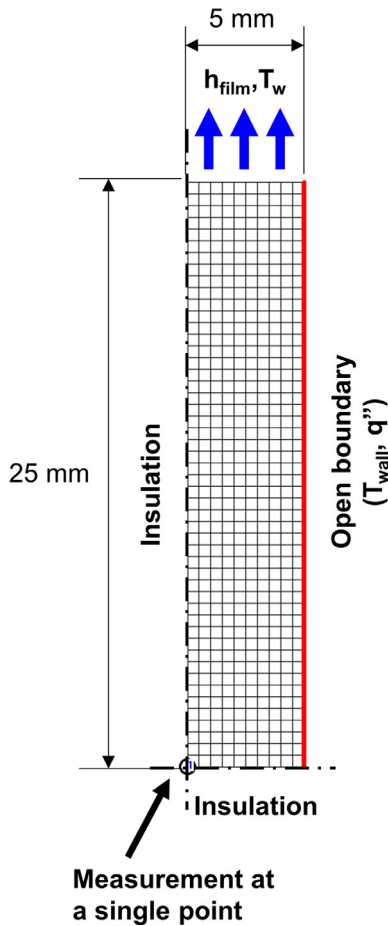


Fig. 5. Problem definition for INTEMP model in the present study.

Table 2
Thermal conductivity, density, and specific heat of Zircaloy [34].

Thermal properties	Correlation
Thermal conductivity (W/m·K)	$k = 12.767 - 5.4348 \cdot 10^{-4} \cdot T + 8.9818 \cdot 10^{-6} \cdot T^2$ (300 K < T < 1800 K)
Density (kg/m ³)	$\rho = 6595.2 - 0.1477 \cdot T$ (<1083 K)
Heat capacity (J/kg·K)	$C_p = 255.66 + 0.1024 \cdot T$ (273 K < T < 1100 K)

coefficient (200 W/m²·K, [4]) with a constant external temperature. The inner boundaries were symmetry conditions, and heat conduction in the angular direction was neglected. Due to the ill-posed problem, conventional uncertainty analysis for the estimation is difficult. Since the uncertainty mainly stems from noise reduction process (i.e. smoothing process) in output data, an effect of the smoothing factor on estimated boiling curves were investigated. The estimated boiling curve in film boiling regime with the optimal smoothing process was consistent with a result of the lumped capacitance method (see Appendix A). Moreover, Kang et al. [16] reported a minimal uncertainty in the INTEMP estimation.

Quenching experiments induced formation of a thin oxide layer due to a high oxygen affinity of zirconium at high temperatures, which is considered in the inverse heat conduction problem. Estimated surface temperature with a thick ZrO₂ layer (50 μm) using the INTEMP model was compared to those without an oxide layer. The result showed negligible difference of surface temperature between the two conditions so INTEMP calculations in the present study were performed under the non-oxidation assumption for

simplicity of the calculation. Thermal properties for ZrO₂ were embedded in the calculation as shown in Table 3. Detail supports of the INTEMP model is discussed in the literature [19].

3. Results and discussion

3.1. Measurement of $T_{\min}$ for bare surface

An initial set of tests used bare Zirc-4 rodlets quenched in saturated water at atmospheric conditions, all at nearly identical conditions to assess reliability and repeatability of the experiment. Reproducibility of the cooling curves was confirmed with ten quenching tests. Based on the results, experimental uncertainties for $T_{\min}$ and minimum film boiling heat flux in saturated water at atmospheric pressure were ± 3 K and 9% of an average value, respectively.

Minimum film boiling temperature was determined based on Carey's definition that it is the surface temperature when the minimum surface heat flux in a boiling curve with sustaining stable film boiling regime is reached [22]. In addition, radiation heat transfer was ignored in the progress of determining the minimum film boiling point due to its small contribution to the total heat transfer. In saturated water at atmospheric pressure, the measured minimum film boiling temperature and minimum film boiling heat flux for bare surfaces were 325 ± 6 °C and 45 ± 4 kW/m², respectively. The result is reasonably in good agreement with published quenching experiments for the similar geometry of zirconium samples at the reference condition (e.g. $T_{\min} = 324$ °C [16] and $T_{\min} = 388$ °C [23]). However, it is worth noting that there are deviations of minimum film boiling temperature in the past literature [4,5], which is attributable to different sample geometry, experimental method, a criterion of $T_{\min}$ determination, various surface conditions. For example, Nishio and Uemura [24] pointed out that total collapse of vapor film can be triggered by a precursory local destabilization on a weak spot like a supporting stem connecting to spherical or cylindrical samples.

3.2. Surface effects in atmospheric saturated water

Quenching experiments for the cylindrical Zirc-4 samples with the surface modifications were carried out at least three times in saturated water at atmospheric conditions. In Fig. 6, both the quenching and boiling curves for the modified surfaces are plotted. The bare surface cooled from the initial temperature to equilibrium conditions the slowest while the roughened surfaces took the quickest to cool. During initial quenching, the rough surface showed larger cooling rates compared to the bare surface and the pre-oxidized surfaces, corresponding to the large surface heat flux at high superheats in the boiling curve. It is interesting to note that surface heat flux for the rough surface increases as the cooling process continues at high superheat. This observation contradicts the classical trend of a boiling curve in the stable film boiling regime – surface heat flux decreases with decreasing surface superheat due to thinning of the vapor layer. The phenomenon shown in the rough surfaces is called a “climbing effect” in the present study. The climbing effect has been reported in the previous literature performing quenching tests of modified surfaces. Fan

Table 3
Thermal conductivity, density, and specific heat of ZrO₂.

Thermal properties	Value
Thermal conductivity (W/m·K)	$k = 2.00$ [35]
Density (kg/m ³)	$\rho = 5680$ (273 K) [36]
Heat capacity (J/kg·K)	$C_p = 455$ (273 K) [37]

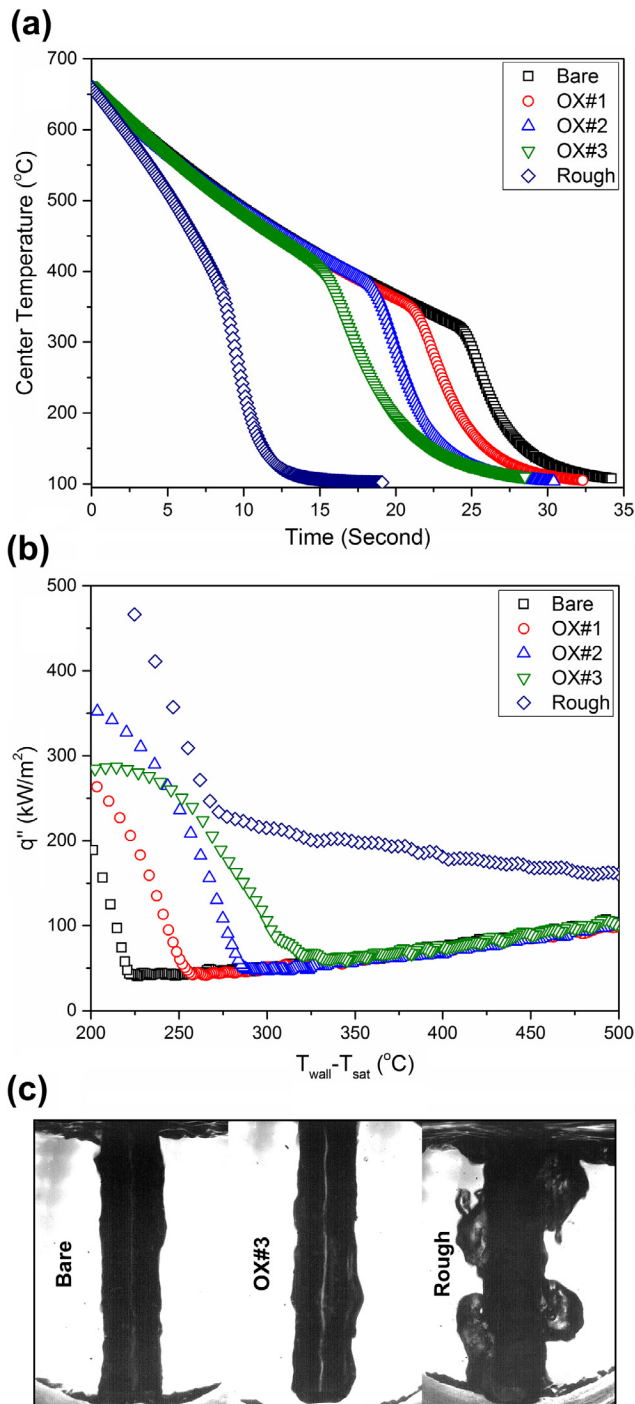


Fig. 6. (a) Quenching curves, (b) boiling curves, and (c) high-speed images (100 fps) of the bare surface, the pre-oxidized surfaces, and the rough surface in saturated water at atmospheric pressure.

et al. fabricated a superhydrophilic surface (water contact angle $\sim 0^\circ$) on a 304 stainless-steel sphere using a silica nanoparticle deposition [15]. The boiling curve for the modified surface showed the climbing effect during quenching in saturated water at atmospheric pressure, and the authors proposed that the nanoparticle deposited surface had a minimum film boiling point higher than an initial surface superheat (200 K). In addition, micro-porous CuO structures (100 μm in height) on a brass sphere were prepared and the climbing effect was presented in the boiling curve for the micro-structured surface in atmospheric saturated water [6]. This

study assumed that the modified surface had a T_{min} point higher than the highest surface temperature (600 °C). Therefore, it is reasonable to assume that the enhanced surface roughness in the present study led to an increase in the minimum film boiling temperature above the initial sample temperature (700 °C) and the climbing effect was an indicative of the transition boiling regime.

Additionally, the cooling performance was improved with increasing thickness of the oxide layer on the surface. The inflection point in the quenching curves was identified at higher temperature as thickness of the oxide layer increases; the minimum film boiling temperature for OX#1, OX#2, and OX#3 were $355 \pm 10^\circ\text{C}$, $392 \pm 9^\circ\text{C}$, and $432 \pm 6^\circ\text{C}$, respectively. Since all the oxidized samples had smooth surfaces ($R_a < 0.3 \mu\text{m}$), it is believed that the surface thermal properties are important factors in determining the transition point in transient boiling heat transfer.

Observation of film dynamics was helpful to elucidate the distinct boiling curves depending on the surface conditions. Snapshots of the hot samples just submerged in the water are presented in Fig. 6c. The pre-oxidized sample (OX#3) shows the stable vapor film regime, consistent with the classical bubble dynamics. However, film dynamics for the rough surface were dissimilar to those for the smooth surfaces. The rough surface reveals fluctuation of the vapor layer is so strong that small bubbles escaped from the thick vapor layer even in the highest wall superheat. The stable film boiling regime is not identifiable, but the vigorous vapor generation continues, displayed for the bare surface and pre-oxidized surface conditions in the transition boiling regime. This observation is consistent with the study done by Dasgupta et al. [25] about vapor film behavior on local roughened surface. The authors reported that a local path consisting of numerous small bubbles was identified only on roughened surface while other smooth areas maintained continuous vapor film.

In short, there was no distinct stable film boiling regime in the rough surface conditions during the experiments.

3.3. Surface effects in pressurized and subcooled conditions

Fig. 7 summarizes T_{min} for the bare surface and the pre-oxidized surface (OX#3) under atmospheric water, the pressurized condition (in saturated water at 0.5 MPa. The pressure was maintained with a fluctuation of 0.4×10^{-2} MPa) and the subcooled condition ($\Delta T_{\text{sub}} = 15$ K and atmospheric pressure). The environmental conditions significantly influence quenching behavior; the minimum film boiling temperature increased regardless of the surface conditions compared to those under atmospheric water. In addition, enhanced cooling performance was also provided by the surface oxidation. The minimum film boiling temperature for the bare surfaces and the pre-oxidized surfaces (OX#3) in the pressurized condition were $551 \pm 8^\circ\text{C}$ and $625 \pm 3^\circ\text{C}$, respectively. In the subcooled condition, the minimum film boiling point for the bare surfaces and the pre-oxidized surfaces are $487 \pm 10^\circ\text{C}$ and $589 \pm 1^\circ\text{C}$, respectively. The transition point for the rough surfaces was assumed to exist above the initial sample temperature (700 °C) because the climbing effect is observed in the boiling curves [19]. In conclusion, the surface modifications (i.e., surface oxidation and surface roughness) are responsible for the enhancement of boiling heat transfer during quenching tests in atmospheric saturated water, which are qualitatively consistent with the pressurized condition and the subcooled water condition.

3.4. Liquid-solid contact in stable film boiling

The modified surfaces enhanced cooling performance (e.g. increasing the minimum film boiling temperature) even in the high pressure and the subcooled conditions. Particularly, vapor film

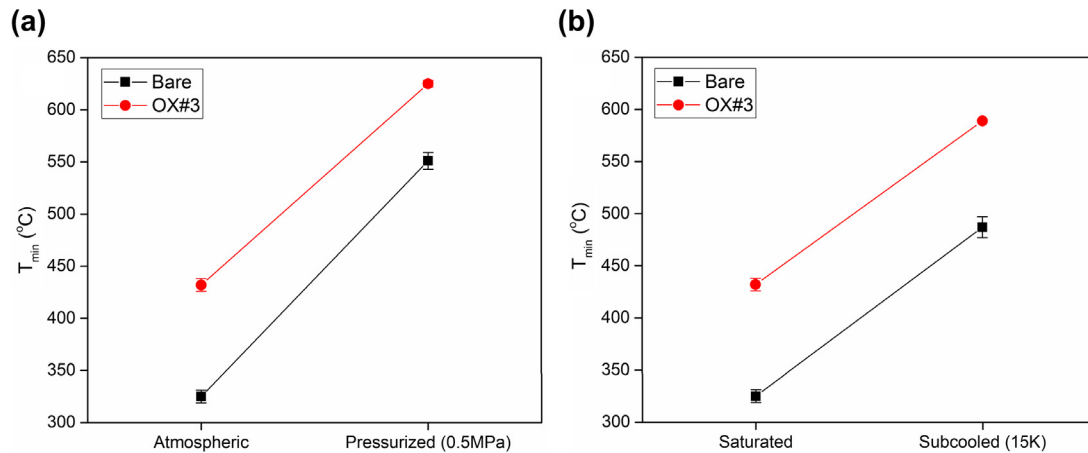


Fig. 7. Minimum film boiling temperature for the bare surfaces and the pre-oxidized surfaces (OX#3) in the three experimental conditions – atmospheric water, (a) saturated water at 0.5 MPa, and (b) atmospheric subcooled water ($\Delta T_{sub} = 15$ K).

dynamics were strongly affected by the surface roughness, leading to the large surface heat flux in the early quenching process. It is hypothesized that effects of the surface characteristics on transient boiling heat transfer correlates with direct liquid–solid contacts on local portions of solid surface. Suppose that the intermittent liquid–solid contact exists during the stable film boiling regime. If this were true, a large amount of heat transfer would be anticipated due to a large temperature gradient between the liquid and hot solid surface. This may trigger destabilization of the stable vapor film if the local surface temperature during the contact is lower than a certain temperature. This characteristic temperature is assumed to be the homogenous nucleation temperature of water ($T_{hm} \sim 305$ °C at atmospheric pressure [3]). The assumption that an intermittent liquid–solid contact occurs during the stable film boiling regime appears to be counter-intuitive if surface temperature is higher than the critical temperature of water (374 °C [26]) because the liquid phase of water is thermodynamically unstable above the critical temperature. Nevertheless, experimental data showing liquid contacts on superheated solid surfaces within the film boiling regime were reported by Dhuga and Winterton [27], and Kikuchi et al. [28].

A rendering of this hypothesis is presented in Fig. 8 to explain a lower limit of the stable film boiling point depending on the postulated surface conditions. There is an intermittent liquid–solid contact in the stable film boiling regime so that the vapor–liquid interface approaches the local solid surface. When the cold liquid rushes toward the surface, a removal of heat from the local area occurs primarily by heat conduction from the solid to the liquid. If the surface temperature is higher than the homogenous nucleation point of water, the liquid cannot wet the solid surface and the liquid front is quickly vaporized. Finally, the continuous vapor film is recovered under the assumption that interfacial disturbance is neglected. Otherwise, the local surface temperature falls below the characteristic temperature (T_{hm}) and, even if the average surface temperature is quite high, the liquid wets the local portion of the solid surface and is evaporated rapidly. Finally, the rate of vapor generation increases at the local area, resulting in improved total heat transfer. The discontinuity of the vapor layer indicates destabilization of stable film boiling. The average surface temperature at which the local surface temperature falls below T_{hm} is defined as minimum film boiling temperature. It is proposed that a thick oxide layer or surface features on the heated surface amplifies the fluctuation of local surface temperature during the direct liquid–solid contact. Thus, the surfaces can have a higher minimum film boiling temperature than the bare surfaces.

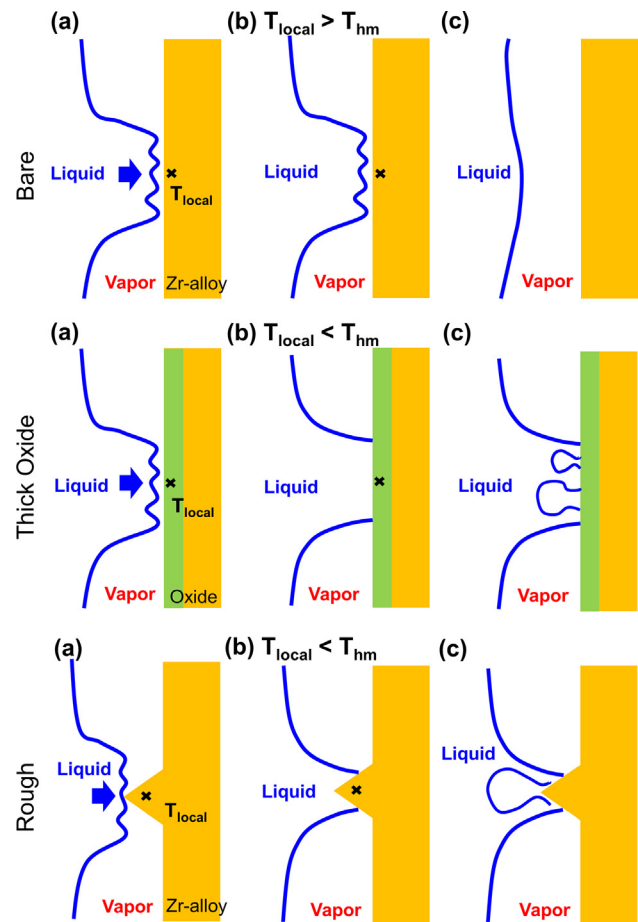


Fig. 8. Schematic illustration of hypothesized bubble dynamics during a liquid–solid contact at high wall superheat depending on surface characteristics: bare surface, surface with a thick oxide layer, and surface feature on the bare surface.

To estimate the thermal response of the solid surface during a simulated liquid–solid contact, assumptions for parameters of the contact such as frequency of the liquid–solid contact, surface heat flux values during the contact, a liquid contact area, and a duration of liquid contact are required. Frequency of liquid–solid contacts in stable film boiling regime was measured by previous researchers. A silver sphere of 20 mm in diameter coated by

electrical insulation paint was quenched under atmospheric saturated water [28]. Measured impedance across vapor layer and the insulating layer to water environment was converted to a frequency of liquid–solid contacts. Kikuchi et al. concluded that the frequency of contacts was ranged from one to three contacts per second at high wall superheats (350–500 K). Additionally, Lee and Chen [29] reported that the frequency of liquid–solid contacts on a horizontal copper surface was approximately 3 contacts/s at high wall superheat (200 K) in atmospheric saturated water. The number of contacts increased to 50 contacts/s as a breakdown of the stable vapor film was observed. In summary, the liquid–solid contact exists in stable film boiling regime but its frequency is extremely low.

Since the liquid–solid contacts appear to occur randomly over heated surface for a short period in the film boiling regime, it is difficult to measure surface heat flux during the liquid contact by quenching experiments. Instead, experiments of water droplets impingement on heated surfaces have been used to estimate the surface heat flux values as an analogy to the heat transfer mode in quenching experiments. Makino and Michiyoshi [30] measured the local surface temperature on mirror polished metal surfaces when a water droplet impacted on the superheated surfaces ($\Delta T_{\text{sup}} = 50\text{--}250\text{ K}$). The authors reported that the highest surface heat flux was on the order of 10^7 W/m^2 during the liquid–solid contact. Chen and Hsu [31] estimated average heat flux with a water droplet of 80°C contact at atmospheric pressure by measuring transient thermal response on preheated Inconel plates using a highly sensitive microthermocouple probe. Instantaneous surface heat flux had a linear function of wall superheats as below. Chen's surface heat flux data were used in the present study.

$$q'' = 51.1\Delta T_{\text{sup}} - 2.72 \cdot 10^3 \text{ [kW/m}^2\text{]} \quad (1)$$

Measured liquid contact areas on a horizontal gold plated surface during film boiling in saturated water at atmospheric pressure were reported by Yao and Henry [3]. The instantaneous liquid contact area was estimated by measurements of electrical conductance between the boiling liquid globule and the solid heater. The authors reported that measured liquid contact area was between $1.1 \cdot 10^{-5}\text{ cm}^2$ to $1.5 \cdot 10^{-5}\text{ cm}^2$ in the range of 200–300 K wall superheats. A diameter of this area would be approximately $40\text{ }\mu\text{m}$ if the area had a circular shape. This diameter was used for the simulation of a liquid–solid contact in the current study.

Durations of liquid–solid contacts were measured during quenching of pre-heated horizontal copper block (720 K) in saturated water at atmospheric condition by Lee and Chen [29]. Average contact duration decreases monotonically with increasing surface superheat. The authors reported that the average liquid–solid contact durations hovered around one millisecond with high wall superheats ($\Delta T_{\text{sup}} = 80\text{--}200\text{ K}$), and increased to 15 ms rapidly before complete contact with the heated surface. At an average surface superheat of 115 K, 97% of the liquid contacts were less than four milliseconds in the experiments. Therefore, the contact duration of three milliseconds was used as a condition in a thermal analysis in this study.

3.5. Prediction of minimum film boiling point

Thermal response of solid surfaces during the simulated liquid–solid contact was estimated to demonstrate the effects of surface properties on quenching behaviors. Transient heat conduction models are prepared using analytical models and commercial heat conduction software, COMSOL (version 4.4). The problem of transient heat conduction in a semi-infinite medium with a thin surface layer of thickness δ_{ox} or a triangular cone of height h_{fin} is schematically illustrated in Fig. 9. It is assumed that a liquid

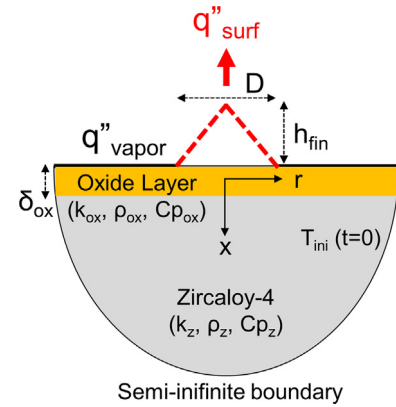


Fig. 9. Schematic illustration of half space with an oxide layer or with a triangular surface feature (red dots). Axisymmetric surface heat flux (q''_{surf}) with the diameter (D), simulating instantaneous liquid contact on the surface, is assumed. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

contact occurs on a circular area of diameter D for a short time (τ_w) with a large constant surface heat flux (q''_{surf}) and the other area is applied by a low vapor heat flux (q''_{vapor}). Thermal properties (ρ , C_p , and k) for the base material (i.e., Zircaloy-4) and the oxide layer (ZrO_2) were assumed to be temperature-independent in this analysis. In addition, thermal radiation is neglected, and a perfect thermal contact between the oxide layer and the base material is assumed. However, it is difficult to find an exact solution for the two-dimensional transient heat conduction problem with a layered system and the boundary conditions using a separation of variables and green function techniques. Only exact solution of a two-dimensional transient heat conduction for semi-infinite solid insulated except for the disk $0 < r < R$ (i.e. bare surface) is reported by Carslaw and Jaeger [32], and Beck et al. [33]. Integral form of the solution is:

$$T(r, x, t) = T_{\text{ini}} + \frac{q''}{2Rk} \int_0^\infty \frac{J_0(\lambda r) J_1(\lambda R)}{\lambda} \left\{ e^{-\lambda x} \text{erfc} \left[\frac{x}{2\sqrt{\alpha t}} - \lambda \sqrt{\alpha t} \right] - e^{-\lambda x} \text{erfc} \left[\frac{x}{2\sqrt{\alpha t}} + \lambda \sqrt{\alpha t} \right] \right\} d\lambda \quad (2)$$

where J_0 and J_1 are the Bessel functions of the first kind of order zero and first. α and k are heat diffusivity and thermal conductivity of a solid, respectively. R is the radius of liquid contact area. The complementary error function, $\text{erfc}(x)$, is defined as:

$$\text{erfc}(x) = 1 - \text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-\eta^2} d\eta \quad (3)$$

The temperature at a center point $(0, 0, t)$ in Eq. (2) is simplified as follows:

$$T(0, 0, t) = T_{\text{ini}} + \frac{2q''\sqrt{\alpha t}}{k} \left\{ \frac{1}{\sqrt{\pi}} - \text{ierfc} \left(\frac{R}{2\sqrt{\alpha t}} \right) \right\} \quad (4)$$

where $\text{ierfc}(x) = \frac{1}{\sqrt{\pi}} e^{-x^2} - x[1 - \text{erf}(x)]$ and this term in Eq. (4) corresponds to an effect of lateral heat diffusion.

Two-dimensional transient thermal problem for the oxidized surface and the rough surface was demonstrated numerically. The triangular surface feature, simulating the rough surface, has $40\text{ }\mu\text{m}$ of height and $40\text{ }\mu\text{m}$ of diameter. The heat conduction model is a cube of $600\text{ }\mu\text{m}$ in each length, which is large enough that semi-infinite media assumption is valid. The surface heat source is applied at a local area of the top surface (a circular shape of $40\text{ }\mu\text{m}$ in diameter) for the pre-oxidized surface and at the outer surface of the conical structure in the case of the rough surface

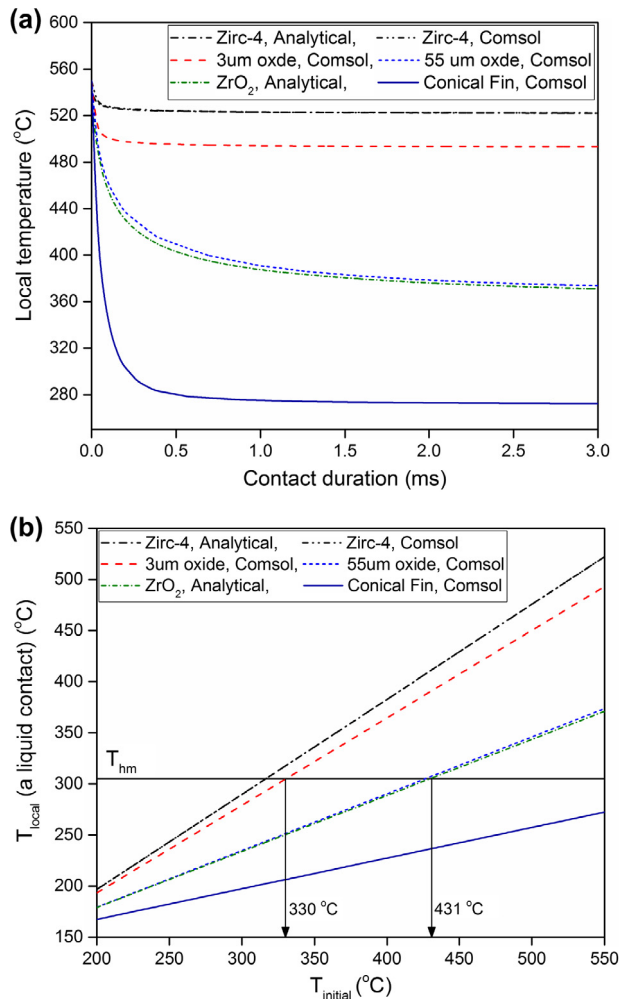


Fig. 10. (a) Temperature transient (if the initial temperature is 550 °C) and (b) the minimum surface temperature at the center of liquid contact area for different surface conditions as a function of the initial temperature of the model, calculated by the analytical model and COMSOL. Duration of the contact was 3 ms and contact diameter was 40 μm. The black arrows indicate the initial temperature when the local temperature for the contact area equals to the homogeneous nucleation temperature of water at atmospheric pressure.

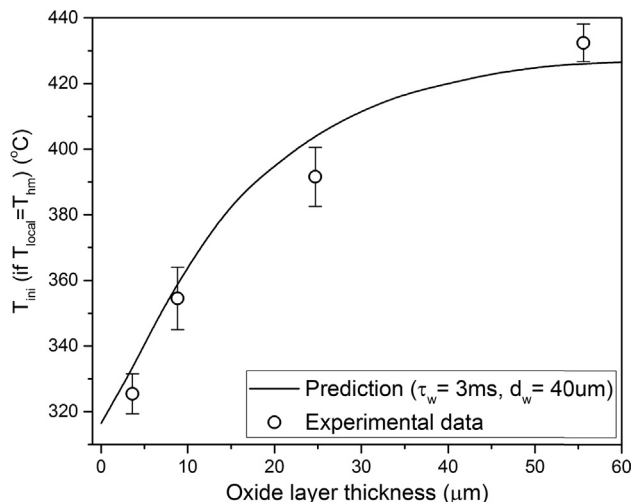


Fig. 11. Predicted and measured minimum film boiling temperatures with different thickness of ZrO₂ layer on Zirc-4 solid in saturated water in atmospheric pressure.

condition. This value is based on Chen's data [31]. The vapor covered surface in stable film boiling is simulated by applying a constant surface heat flux (85 kW/m²) on the top surface except for the liquid contact area. The surface heat flux is the value measured experimentally for bare samples at 450 K wall superheat in atmospheric saturated water where the entire surface is covered by a continuous vapor layer. The bottom surface in the model maintains the initial temperature and four of the side surfaces are thermally insulated. Initial temperature of the model is varied from 550 °C to 200 °C.

Fig. 10a shows the transient temperature drop from the initial temperature at the center of liquid contact area in the postulated surfaces during the liquid contact, and Fig. 10b displays the minimum surface temperature as a function of an initial temperature. Temperature drop for the bare surface is the smallest in the conditions because the heat removal during the contact is readily recovered by lateral heat conduction. The analytical model and the numerical model for the bare surface produces the identical results, proving a reliability of results of the models. If thickness of ZrO₂ layer becomes very thick (i.e., 55 μm in thickness), the result is almost identical to that of bulk ZrO₂. As shown in Fig. 10b, the minimum surface temperature of the triangular fin is the lowest in all surface conditions in the entire range of initial temperature, which is attributed to the increased surface area over which the heat flux is applied and the localized heat conduction. The result may explain the vapor film dynamics of the rough surfaces at high wall superheats during the quenching experiments. The surface temperature of the microstructures on the rough surfaces would be much lower than the average temperature measured by the thermocouple at the center of the sample. Therefore, local surface area (an extruded area) is wetted by cold water, leading to generation of vigorous vapor and large surface heat flux. It is worth noting that the initial temperatures for the surfaces with 3 μm and 55 μm oxide layer, when the local temperatures after the liquid contact equal to the homogeneous nucleation temperature of water, are very close to the measured minimum film boiling temperature for the bare surface and the pre-oxidized surface (OX#3).

With the assumption that the homogeneous nucleation temperature of water is the minimum film boiling temperature on a local area, calculated T_{min} given the parameters of liquid–solid contact and the measured temperatures in atmospheric saturated water are plotted as a function of thickness of ZrO₂ layer in Fig. 11. The experimental results agree well with the theoretical predictions. The predicted curve displays that minimum film boiling temperature increases sharply with the initial development of the oxide layer on bare surfaces, and finally has the asymptotic behavior with further increases in thickness of the oxide scale. It infers that the minimum film boiling point of oxidized surfaces approaches that of bulk ZrO₂ if the oxide scale continues to grow on the surface. The deviation between the predicted curve and experimental data could be attributed to the assumptions in the theoretical models such as a density of the oxide layer, no thermal resistance in the interface between the oxide layer and the Zirc-4 solid, and the conditions of the liquid contact. As shown in Fig. 12, the predicted minimum film boiling temperature increases with longer duration of the direct contact, particularly in the thick oxide layer region due to a large contribution of the oxide layer with the small thermal diffusivity to the entire heat transfer calculation. In the thin oxide layer region (<20 μm), there are a weak dependency of the contact duration on the prediction of minimum film boiling temperature. Therefore, the proposed model is reasonably robust under varying liquid contact durations on the zirconium-alloy surfaces. The liquid contact area has a stronger sensitivity to the prediction than the liquid contact duration. Additional information of sensitivity of the liquid contact parameters is explained in the

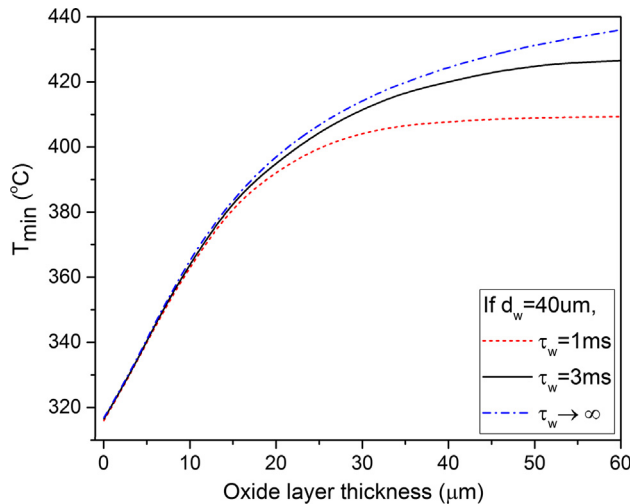


Fig. 12. An effect of liquid contact duration on prediction of minimum film boiling temperature depending on thickness of ZrO_2 layer on Zirc-4 solid in saturated water in atmospheric pressure.

literature [19]. In addition, the strong dependency of $T_{\min}$ on thickness of the oxide layer cannot be explained by Henry's model [2]. Henry proposed that $T_{\min}$ would be correlated with the interfacial temperature between cold liquid and hot solid surface during a liquid contact, but the temperature is determined without the consideration of thickness of the oxide layer. In short, the assumptions and formulations of the present transient heat conduction model appear to be valid when demonstrating the effects of surface oxidation and surface roughness on minimum film boiling temperature in atmospheric saturated water. Accurate measurement of liquid–solid contact parameters such as contact duration, contact heat flux, and contact area at different environmental conditions would be useful for prediction of the minimum film boiling point under the pressurized or subcooled conditions.

4. Conclusion

In this paper, transient pool boiling of cylindrical Zircaloy-4 samples with surface modifications was investigated at various system conditions. The effect of elevated pressure and water subcooling on the quenching behavior of samples was examined by measurements of temperature vs. time at the center of the samples as well as visualization of vapor dynamics and evolution. Boiling curves were plotted by inverse heat conduction analysis of the measured temperatures. Modified surfaces of Zircaloy-4 were prepared by oxidation of the samples at 700 °C in air with different exposure times (oxidized surfaces) and by grit blasting (rough surface) prior to repeated quenching experiments. Classical boiling regimes were observed for the bare clean surfaces in atmospheric saturated water. The oxidized surfaces and the rough surfaces enhanced quenching performance in the system conditions (i.e., in atmospheric saturated water, in saturated water at 0.5 MPa, and in atmospheric 15 K subcooled water). An accelerated transition of boiling regimes occurred due to the surface oxidation and the surface roughness. Improvement of boiling heat transfer in high wall superheats was achieved by the increase in surface roughness. Vapor film dynamics were strongly affected by rough surfaces and stable film boiling regime was not observed in the study. In addition, a plausible hypothesis based on instantaneous heat transfer during liquid–solid contacts during the film boiling regime was proposed to explain the enhanced boiling heat transfer by the surface modifications. The two-dimensional transient heat

conduction model with given assumptions elucidates the film dynamics qualitatively depending on the surface conditions and predicts the minimum film boiling temperature of the oxidized surfaces. These results are in good agreement with the experimental results. It suggests that both surface properties and parameters of liquid–solid contact are dominant factors in controlling transient pool boiling heat transfer during water quenching.

Conflict of interest

The authors declare that there is no conflict of interest.

Acknowledgment

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Appendix A

As mentioned in the text, the inverse heat transfer problem used measured temperatures at a specific location (e.g. centerline) inside the solid and the symmetry condition at the centerline as boundary conditions. This problem is known as ill-posed problem as introduced in the literature [10,38–40]. Differing from a well-posed problem (stable and unique solution exists), a solution of the ill-posed problem was not stable so that arbitrary small changes in the temperature measurement at the centerline amplifies in the projection to the unknown surface condition. Therefore, prediction of the surface heat flux could be overwhelmed – jagged heat flux data. Thus, INTEMP offers a smoothing process to eliminate the noise in the output heat flux data. Trujillo and Busby [38,39] introduced a dynamic programming filter which optimally smoothing the output data using a third-order filter. The basic concept is building a cubic spline function passing near output data points with maintaining a certain degree of smoothness and minimizing a deviation from the output data. The degree of smoothness is controlled by a smoothing factor (SF) in INTEMP model. Detailed explanation for the smoothing process are specified in the literatures [20,21]. Sensitivity analysis for the smoothing factor to boiling curves for a bare Zirc-4 specimen at ambient conditions were performed. As shown in Fig. A1, estimated boiling curve

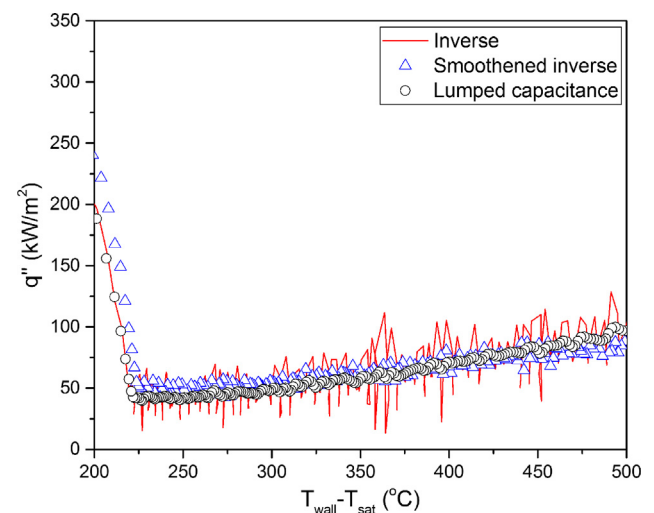


Fig. A1. Boiling curves of bare Zirc-4 calculated by two-dimensional INTEMP analysis and a lumped capacitance method.

without the noise reduction showed strong oscillations but the curve with a proper smoothening process displayed good agreement with the lumped capacitance method, when in the film boiling regime. Since the maximum heat flux (i.e. Critical heat flux) and nucleate boiling regime were strongly influenced by the noise reduction process such as a loss of heat flux data and over-smoothing, the result was excluded in the post-data processing. In short, it can be concluded that the two-dimensional INTEMP calculation is useful and reliable to estimate surface heat flux and surface temperature while eventually being utilized to evaluate $T_{\min}$.

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DEVELOPMENT OF ZIRCONIUM-SILICIDE COATINGS FOR ACCIDENT TOLERANT ZIRCONIUM-ALLOY FUEL CLADDING

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ABSTRACT

Transition metal silicide compounds are generally known for their outstanding oxidation resistance at high temperatures. In this paper, we present our initial investigations on zirconium-silicide as a potential candidate coating material for enhancing accident tolerance of zirconium-alloy fuel cladding used in light water reactors. Results of oxidation performance of bulk ZrSi₂ in ambient air at 700 °C, 1000 °C, and 1200 °C are first presented. Following this, results of oxidation tests of ZrSi₂ thin film coating deposited on Zircaloy-4 test flat substrates in ambient air at 700 °C are discussed. The thin film coatings were deposited using the physical vapor deposition (PVD) method, at room temperature. Samples from the above tests were analyzed using scanning electron microscopy in conjunction with energy dispersive spectroscopy and focused-ion beam sectioning, x-ray diffraction, and x-ray photoelectron spectroscopy. The results clearly demonstrate the outstanding oxidation resistance of ZrSi₂, while coatings of this material exhibit superior oxidation resistance compared to the uncoated Zircaloy-4.

I. INTRODUCTION

Zirconium-alloy (Zr-alloy) has been successfully used as fuel cladding material in Light Water Nuclear Reactors (LWR) for decades due to its low neutron absorption, and a combination of good mechanical and corrosion properties under normal LWR operation conditions. However, at high temperatures, as for example might be experienced in a loss of coolant accident (LOCA) condition, Zr-alloy undergoes profuse exothermic oxidation leading to thick oxide scale formation with hydrogen gas release due to reaction between Zr-alloy with water or steam. One option to improve safety margin during one of accident scenarios and to enhance performance under normal operating conditions, is to apply of surface

modification and coating treatments Zr-alloy cladding that will improve its oxidation resistance.

In this study, the potential for the use of zirconium-silicide coatings on Zr-alloy has been investigated. The literature for the degradation of MoSi₂, a well-known high temperature coating material¹, suggests that Zr-silicides might exhibit superior performance during high-temperature accident conditions. Zr-silicides are preferred over MoSi₂ because the Zr-silicide layer is expected to bond more strongly to the inner, native ZrO₂ layer. Additionally, an examination of the Zr-Si binary phase diagram indicates multiple intermetallic compounds which suggests which under high temperature oxidative conditions a Zr-silicide compound can naturally evolve into a compositionally and functionally graded multilayered system of ZrO₂ and SiO₂ sandwiched layers that can potentially provide the necessary protection under accident conditions. This multi-layered structure, it is believed will have the potential to degrade during irradiation in a way that enhances the protective nature of the barrier layer through self-healing and transport-limiting processes. Depending on the environmental conditions, a highly corrosion-resistant amorphous zircon (ZrSiO₄) layer can also form on the surface.

With the above background, this paper reports our initial work on oxidation behavior of bulk ZrSi₂ and thin film coating of ZrSi₂ deposited on Zr-alloy.

II. EXPERIMENTAL PROCEDURE

Bulk ZrSi₂ samples produced by consolidation and sintering were procured from American Elements Inc., Los Angeles, CA. It has a high purity (>99.5% metal basis) but some micron size free silicon particles were identified in the ZrSi₂ matrix as an impurity. The ZrSi₂ thin film was deposited on test flats of Zircaloy-4 (referred to as

Zry-4 henceforth) using Denton Discovery 24 Sputtering equipment at the University of Wisconsin. For this deposition work, Zry-4 substrates were cut to a size (12.5 mm x 12.5 mm x 3.17 mm) and ground by 600grit SiC paper followed by ultrasonic cleaning in acetone and methanol. A 76 mm diameter and 3.17 mm thick ZrSi₂ target was used as the target material. The sputter chamber was pumped down to a base pressure of (2×10^{-6} mtorr) prior to deposition. Argon was used as the sputtering gas and deposition was conducted with the Zry-4 samples at room temperature. Sputtering was conducted at a power setting of 135 watts and at an argon gas pressure of 4 mtorr. The resulting thickness of the Zr-silicide coating was about 850 nm.

Test samples of Zry-4 test flats, bulk ZrSi₂, and Zr-Si₂ coated Zry-4 were oxidized in a Lindberg furnace in ambient air environment air at 700 °C for an exposure duration of 5 hours with samples being removed every hour for weight change measurements (as a measure of the extent of oxidation) and analysis. In another experiment, test flats of Zry-4 and bulk ZrSi₂ were oxidized at 1000 °C and 1200 °C also for exposure duration of 5 hours with samples being removed each hour for weight change measurements (as a measure of the extent of oxidation) and analysis.

All samples discussed above were rigorously characterized before and after oxidation tests using suite of characterization methods. Weight change (per unit area) measurements for all samples was performed with a balance with a resolution of 0.002 mg. Scanning electron microscopy (SEM) in conjunction with energy dispersive spectroscopy (EDS) was used to evaluate the surface morphology, thickness, and composition of the coatings as well as the oxide layers formed from high temperature exposures. Grazing incidence x-ray diffraction (GIXRD) and conventional x-ray diffraction techniques were used phase identification in the coatings and oxide layers. Because of the very small thickness of the oxide layers on some of the samples, x-ray photoelectron spectroscopy (XPS) was also applied to characterize the oxide layers.

III. RESULTS AND DISCUSSION

III. A. ZrSi₂ Thin Film Coating

The Zr-Si₂ film deposited on Zry-4 substrates was uniform and relatively defect free and exhibited a bulbous structure typical of PVD coatings (Figs. 1a and b). The coating thickness is as measured by the cross-sectional image acquired by focus ion beam (FIB) milling was 850nm (Fig. 1c). X-ray

diffraction analysis with 2° incident x-ray angle shown in Fig. 1d reveals only the peaks of zirconium substrate peaks not only in the Zry-4 substrate and a faint amorphous signal of the Zr-Si₂ coating. The amorphous structure of PVD films deposited at room temperature is predicted by Thornton's structure zone model³ and has been observed in other sputter coatings deposited at room temperature⁴⁻⁶. Elemental composition of the as-deposited coating was measured by EDS and XPS. The zirconium-to-silicon atomic ratio in the coating was approximately 1:1.9 as determined by EDS and 1:2.4 as determined by XPS. This is reasonably consistent with the sputter target composition (1:2). In short, the Zr-Si₂ amorphous thin coatings were successfully deposited on Zry-4 flat coupons without any significant defects.

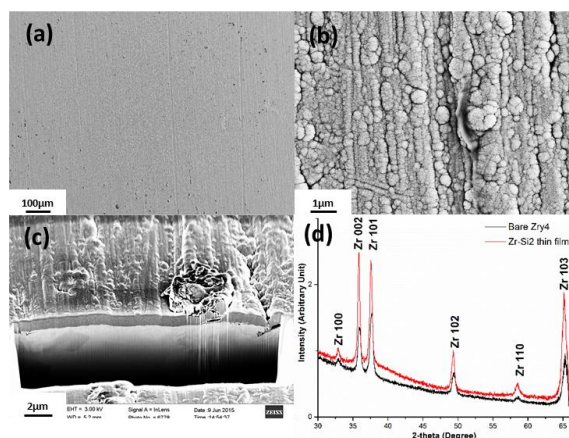


Figure 1: SEM examination Zr-Si thin film coating on Zry-4 (a) low magnification image, (b) high magnification, and (c) cross-sectional image of the coating after focus ion beam sectioning to measure the film thickness, and (d) x-ray diffraction patterns for uncoated Zry-4 and Zr-Si₂ thin film coated Zry-4 taken with 2° grazing angle.

III. B. Oxidation Tests of Thin Film and Bulk Materials

III. B. 1. Oxidation test at 700 °C

The flat bare Zry-4, bulk ZrSi₂, and Zr-Si₂ coating coupons were oxidized at 700 °C dry air for 5 hours and their weight gain (per unit area) by removing samples at 1 hour increments. As seen in Fig. 2, the bare Zry-4 showed the largest weight gain of the three types of materials and weight gain for the bulk ZrSi₂ was almost negligible. It is worth noting that a 33% reduction in weight gain was achieved by the 850 nm Zr-Si₂ PVD coating compared to the uncoated Zry-4, which indicates that the thin coating acts as oxidation barrier.

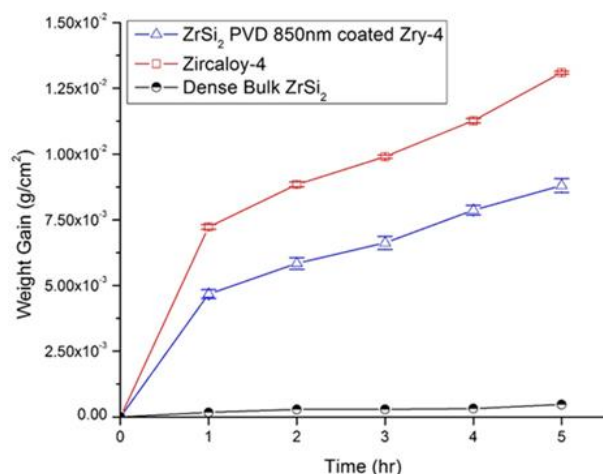


Figure 2: Results of weight gain measurements for the three types of material samples after oxidation tests at 700 °C in ambient air environment.

Plan-view examination of the samples oxidized for 5 hours was performed using SEM to evaluate differences in surface morphology of the oxide layer that develops on the three types of materials (Fig. 3). Mild cracking were identified on the Zr-Si₂ coated sample surface although significant coating damage such as spallation and delamination was not detected. Micron size silicon enriched regions were observed on the surface of bulk ZrSi₂ samples which were not present before the oxidation test. In addition, local variation of elemental composition on the oxidized surface was confirmed by EDS analysis for bulk ZrSi₂ sample. It is speculated that the differences in oxidation thermodynamics and kinetics between zirconium and silicon may lead such partitioning. We are presently evaluating these effects by high magnification SEM and scanning transmission electron microscopy (STEM) and will report the results in a later paper.

In order to measure the thickness of the oxide layer that forms on the various samples, the cross-sectional observation using SEM in the back scattered electron (BSE) imaging mode as well as secondary electron mode was conducted. Using these methods, the oxide layer thickness formed on Zry-4, ZrSi₂ coated (excluding coating thickness), and bulk ZrSi₂ samples was determined to approximately 10 μm, 1 μm, and 470 nm, respectively. The values represent an average value of thickness measured (total 10 measurements each image) at several locations in images such as the ones shown in the red arrows in Figure 4. The cracks observed in the oxide layer formed on bare Zry-4 (Fig. 4a) may be attributed to oxidation-induced stress due to volume change associated with the formation ZrO₂⁷. On the other

hand, the thin Zr-Si₂ coating appeared to strongly impede oxygen diffusion as evidenced by the lack of any oxidation of the underlying Zry-4 substrate (Fig. 4b). As may be noted in this figure, the oxide layer thickness formed on the coating appears inconsistent with the weight gain result. One of the reasons for this is that only the two major surfaces of the substrates were coated. The oxide layer thickness provides a more accurate assessment of oxide layer thickness, and based on this our studies indicate that the weight gain results underestimate the actual oxidation resistance of the coating. In addition, oxidation of the bulk ZrSi₂ was so difficult that its oxide layer was too thin (~470 nm) to observe even on the SEM image (Fig. 4c).

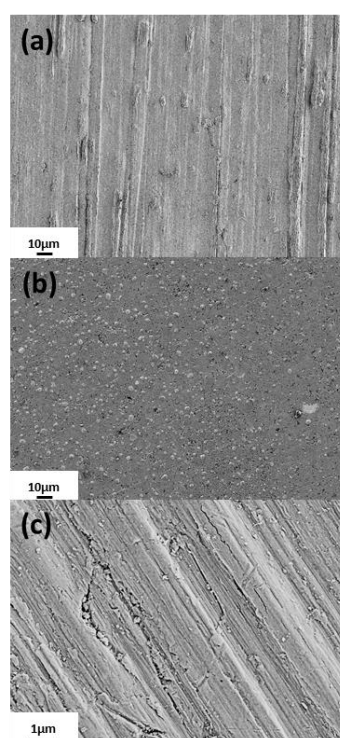


Figure 3: SEM plan-view images of (a) Zr-Si₂ coating surface, (b) bulk ZrSi₂ surface, and (c) Zry-4 after oxidation test at 700 °C for 5 hours.

XRD analysis also showed that the Zr-Si₂ coating protected Zry-4 substrate from oxidation. The intensity of zirconium peaks were preserved in coated samples indicating quite directly that the oxidation of the underlying Zry-4 substrate was drastically mitigated by the coating. In contrast, the ZrO₂ peaks were very pronounced in the uncoated Zry-4 alloy and peaks of elemental Zr was diminished. In addition, near-surface XPS analysis of the Zr-Si₂ coated and bulk ZrSi₂ samples showed that the top surface of the both material samples was fully oxidized as only binding energy from ZrO₂ and SiO₂ were identified.

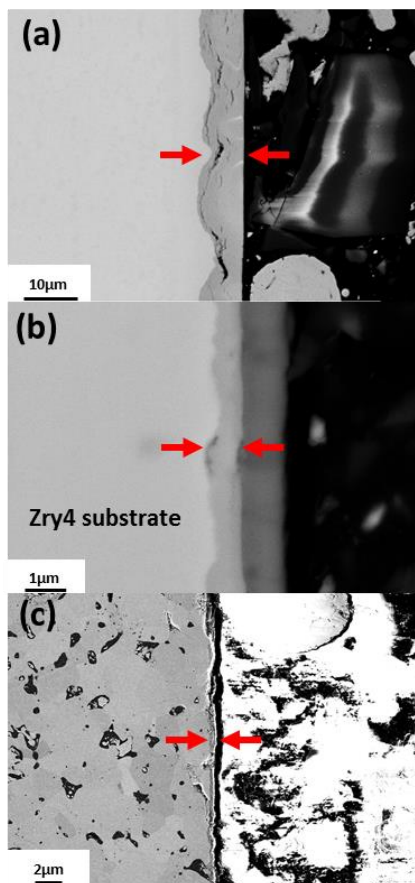


Figure 4: SEM-BSE images of cross section of (a) bare Zry-4, and (b) and Zr-Si₂ coated samples and SEM image of (c) bulk ZrSi₂ after oxidation tests at 700 °C for 5 hours.

III. B. 2. Oxidation Tests at 1000 °C and 1200 °C

To simulate response of zirconium-alloys to LOCA conditions, higher temperature (>1000 K) oxidation in steam or air or the mixture environment has been widely conducted⁷⁻⁹. We plan to conduct these tests as well, but to make an initial assessment of ZrSi₂ to withstand these conditions, coupons of bulk ZrSi₂ and bare Zry-4 were exposed to oxidation tests at 1000 °C and 1200 °C for 5 hours in ambient air environment.

At both temperatures, the weight gain of the bulk ZrSi₂ was very small compared to the bare Zry-4 as shown in Fig. 5. Zry-4 coupons experienced severe oxidation and degradation from breakaway of oxide scale leading to weight reduction at 3 hour oxidation at 1000 °C and 2 hour oxidation at 1200 °C. The edge of ZrSi₂ coupons were also chipped off slightly at 1200 °C 3 hour test so its weight was slightly reduced. But other flat surfaces on the sample appeared to be stable.

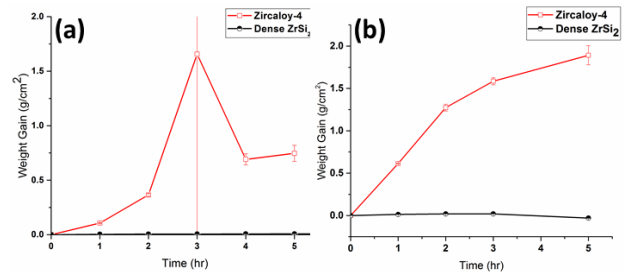


Figure 5: Weight change measurements of bare Zry-4 and bulk ZrSi₂ samples at (a) 1000 °C and (b) 1200 °C.

Plan view SEM images (see Fig. 6) shows that surface roughness of the bulk ZrSi₂ samples increases with increased exposure temperature but no defects such as cracking or delamination were observed in either case. Significant characteristic x-ray signal of oxygen was identified in EDS analysis in the both cases. Oxide layer build up on the top surface during the oxidation seems to be robust free of possible stress mismatch between oxide/unreacted ZrSi₂ which would manifest as spallation.

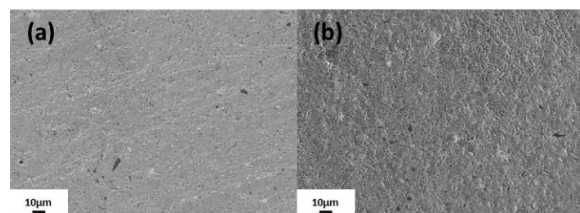


Figure 6: SEM plan-view images of bulk ZrSi₂ samples after oxidation tests at (a) 1000 °C, and (b) 1200 °C for 5 hours.

The cross-sectional SEM images of bare Zry-4 and bulk ZrSi₂ oxidized at 1000 °C (Figure 7) confirm excellent oxidation resistant of ZrSi₂ as a material in this high temperature air environment. The average oxide thickness at 1000 °C for 5 hours evaluated of bulk ZrSi₂ and Zry-4 were about 6.7 µm and 650 µm, respectively. Significant degradation occurred in the bare Zry-4 during the oxidation and a number of cracks perpendicular to oxide/air interface and cracks along with oxide/metal interface were revealed in these cross-sectional examinations. In some regions, the oxide scale was delaminated from the surface. In contrast, the oxide layer on bulk ZrSi₂ was too thin to be observed clearly (Fig. 7b), which indicates the ZrSi₂ to be a promising material applicable to high temperature air environment. In 1200 °C oxidation tests, the 3.17 mm thick Zry-4 coupons were completely oxidized and crumbled but oxide layer thickness of ZrSi₂ was only about 37 µm. The multiple thermal cycles induce thermal stresses in the samples. In particular, degradation of mechanical integrity of

Zry-4 samples would attribute to compressive stress in oxide scale due to the phase transformations in ZrO_2 during cooling. It is concluded that the oxidation resistance was higher by a factor of greater than 100 for bulk ZrSi_2 compared to bare Zry-4 at 1200 °C in terms of oxide layer thickness.

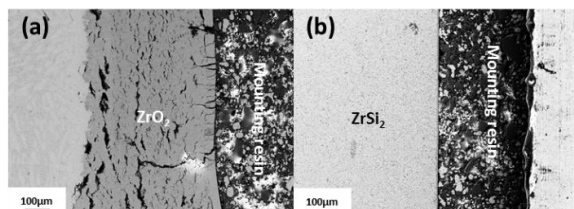


Figure 7: SEM cross-sectional images of (a) bare Zry-4 and (b) bulk ZrSi_2 after oxidation at 1000 °C for 5 hours.

X-ray diffraction analysis of the oxidized bulk ZrSi_2 after both high temperature tests showed strong zirconium oxide peaks, unreacted ZrSi_2 , and weak Si peaks. However at the higher oxidation temperature of 1200 °C, ZrSi_2 signals were weaker and oxide peaks were stronger. The Zry-4 samples oxidized significantly at this temperatures only strong ZrO_2 phase peaks were observed.

IV. CONCLUSIONS

To evaluate the efficacy of Zr-silicide as a potential coating for Zr-alloy cladding for enhanced accident tolerance, the high temperature oxidation behavior of bare Zry-4, 850 nm thick Zr-Si₂ coatings deposited on Zry-4 substrates, and bulk ZrSi_2 were performed in air environment. The oxide layers formed on the various material samples were characterized in detail using SEM-EDS, X-ray diffraction, and XPS techniques. The Zr-Si₂ coatings were deposited using the PVD process with the substrates maintained at room temperature. In 700 °C oxidation tests, performed on the samples of the three materials, an oxide layer thickness of 10 μm, 1 μm, and 470 nm, developed on Zry-4, ZrSi_2 coated, and bulk ZrSi_2 samples, respectively. The thin Zr-Si₂ coatings acted as very effective diffusion barrier for oxygen and dramatically mitigated the oxidation of the underlying substrate. For oxidation tests performed on Zry-4 and bulk ZrSi_2 samples tested at 1000 °C and 1200 °C, the Zry-4 samples exhibited profuse degradation due to oxidation, while a relatively thin mechanically stable oxide developed on bulk ZrSi_2 samples. For, example in 1000 °C tests for 5 hours, the oxide layer formed on bulk ZrSi_2 samples was 100 times thinner than that formed on uncoated bare Zry-4. These results support that the candidacy of Zr-silicide as a protective coating material on Zr-alloy

cladding under LOCA conditions. The paper demonstrates the feasibility of zirconium-silicide as an accident tolerant coating material on Zr-alloy cladding. Present work is focused on developing an in-depth understanding the oxide layer evolution of PVD Zr-Si thin film and bulk ZrSi_2 both experimentally and theoretically using techniques such as transmission electron microscopy (TEM) and computational modeling.

ACKNOWLEDGEMENTS

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Development of Zirconium-Silicide Coatings for Improved Performance Zirconium-Alloy Fuel Cladding

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INTRODUCTION

There is considerable interest in the development of coatings for zirconium-alloy fuel cladding used in light water reactors (LWR) to improve their oxidation resistance during high temperature accident conditions and to enhance performance under normal operating conditions.¹⁻³ These coatings should also enhance the heat transfer characteristics of the cladding surface so that heat from the fuel rod is efficiently transferred into the water coolant. One potential candidate coating material is zirconium-silicide. Transition metal silicides have been generally shown to have outstanding oxidation resistance.⁴⁻⁷ Zirconium-silicide is particularly attractive because Zr is strongly oxophilic, so that the Zr-silicide layer is expected to bond more strongly to the inner, native ZrO₂ layer. The relative proximity of the free energy of formation of oxides of Zr and Si can lead to alternating multilayered oxide structures with radiation damage resistance. Additionally, oxidation of zirconium silicide can produce excellent corrosion resistant glassy zircon (ZrSiO₄) and silica (SiO₂), possessing self-healing qualities.

This paper reports results of our results of high temperature oxidation tests of bulk zirconium-silicide and coatings of zirconium-silicide deposited on zirconium-alloy test flats and cladding tube configurations using plasma vapor deposition (PVD) process. We also report our initial results on the experimental facility for studying boiling characteristics of coated cladding tubes in prototypic pressurized water conditions

EXPERIMENTAL PROCEDURE**Materials**

In order to investigate oxidation behavior of zirconium silicide, dense ZrSi₂ with a reported purity of >99.5 % has been procured. For PVD work of Zr-silicide coating on Zr-alloy substrate, ZrSi₂ sputter target was procured. The target had dimensions of 76 mm diameter and 3.2 mm thickness with 99.5 % purity with 3.2 mm thick copper backing plate.

For quench tests specimen, 300 mm-length stainless steel 316 (SS316) rod and a 300 mm-length Zr-alloy (Zircaloy-4 grade) rod were procured. The rods were machined to short rodlets (60 mm-length and 10 mm-diameter).

Coating Fabrication

Zirconium silicide coatings were deposited on the Zircaloy-4 (Zirc-4) test flats and tubes using the PVD process (Denton RF/DC Sputter). Prior to deposition, the substrates were polished progressively with 320 grit and 600 grit silicon-carbide abrasive paper followed by cleaning with acetone and methanol. Finally, plasma cleaning (at 500 W for 5 min) was performed in-situ in the sputter chamber just before initiating PVD process. The PVD chamber had a base pressure of $2 \cdot 10^{-6}$ mtorr and sputtering was carried out using argon gas with a flow of 20 sccm. The deposition rate and coating quality was strongly dependent on voltage bias on the cathode target, the argon pressure, deposition time, and substrate temperature.

Oxidation Tests

High temperature oxidation tests of the samples were performed using commercial furnaces (e.g., Lindberg box furnace, model#51442) at the University of Wisconsin. For the ZrSi₂ and Zirc-4 substrate, the samples were polished with 320, 400, and 600 grit SiC papers and then ultrasonically cleaned with acetone and methanol. For the air oxidation test, samples were exposed at 700 °C in ambient air. The samples were removed each hour for weight change measurement (as an initial measure of the extent of oxidation) performed with Satorius micro-precision balance (model#CPA26P) with 0.002 mg resolution.

Pressurized Quench Test

A photograph of the quench test facility designed and built for this research is shown in Figure 1. The facility essentially consists of the following

components: an air actuator, a Teflon seal assembly, a heating zone, a cylindrical test section, a water quenching chamber, and electronics. When the cylindrical test section (Zirc-4 or 316 stainless steel) temperature reaches the desired temperature, the specimen (cylindrical rod) is plunged into the quench chamber with saturated water. The chamber pressure is regulated by pressure regulators using a compressed Argon gas. The temperature variation of the test sample and bubble evolution on the surface during the quench process are recorded. The test is completed when thermal equilibrium is identified between the test section and the water pool.

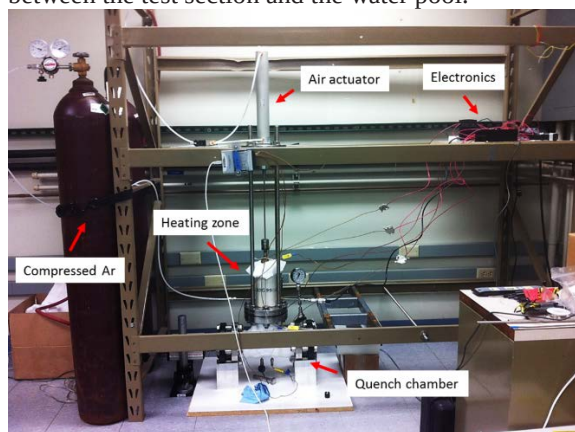


Fig. 1. A photograph of the quench test facility designed and built for this research.

EXPERIMENTAL RESULTS

Oxidation Test

Bulk ZrSi_2 , Zirc-4, and PVD ZrSi_2 coating (about $850\ \mu\text{m}$ thickness) were oxidized at $700\ ^\circ\text{C}$ for 5 hours in ambient air to observe the oxidation behavior. Figure 2 shows the weight gain (per unit area of the sample) of the samples. As may be noted, the weight gain of the dense ZrSi_2 is negligible compared to that of the Zirc-4 at the high temperature. In addition, about 60% reduction in weight gain was achieved by the thin ZrSi_2 coating, which indicates that the thin coating acts as oxidation barrier. Since the bulk ZrSi_2 has much smaller weight gain, the PVD ZrSi_2 coating still has a room for improvement; thinner and less covered coating on the side faces of the samples may attributable to the greater weight gain (this is an inherent artifact of the test and the true measure is therefore the actual examination of oxide layer thickness).

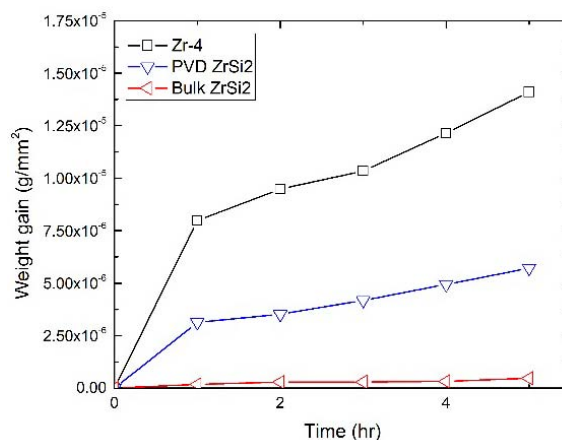


Fig. 2. Results of weight gain of bare Zirc-4, ZrSi_2 coating deposited on Zirc-4, and bulk ZrSi_2 after oxidation tests at $700\ ^\circ\text{C}$ in ambient air.

The oxide layer thickness was measured in SEM cross-sectional images and shown in the Figure 3. The average oxide layer thickness of the Zirc-4, the bulk ZrSi_2 , and the ZrSi_2 coating on Zirc-4 at $700\ ^\circ\text{C}$ for 5-hour oxidation was determined to $13\ \mu\text{m}$, $470\ \text{nm}$, and $1\ \mu\text{m}$, respectively. The oxide layer thickness formed on the bulk ZrSi_2 is in good agreement with the weight gain result compared to that of Zirc-4. On the other hand, the oxide layer thickness on the ZrSi_2 coating was about 92 % smaller than that on bare Zirc-4, which is inconsistent with the weight gain result. One of the reasons for this is that only the two major surfaces of the substrates were coated. The oxide layer thickness provides a more accurate assessment of oxide layer thickness, and based on this our studies indicate that the weight gain results underestimate the actual oxidation resistance of the coating. Furthermore, no spallation and delamination of the oxide layer were observed in the bulk ZrSi_2 and the PVD ZrSi_2 coating. However, circumferential cracks observed in the oxide layer formed on bare Zirc-4 due to thermal stress arising from periodic removal of sample from the furnace. In short, oxygen diffusion through the thin ZrSi_2 coating seems to be greatly reduced indicating that the coating inherently is protective of the Zirc-4 under the condition of the high temperature air environment.

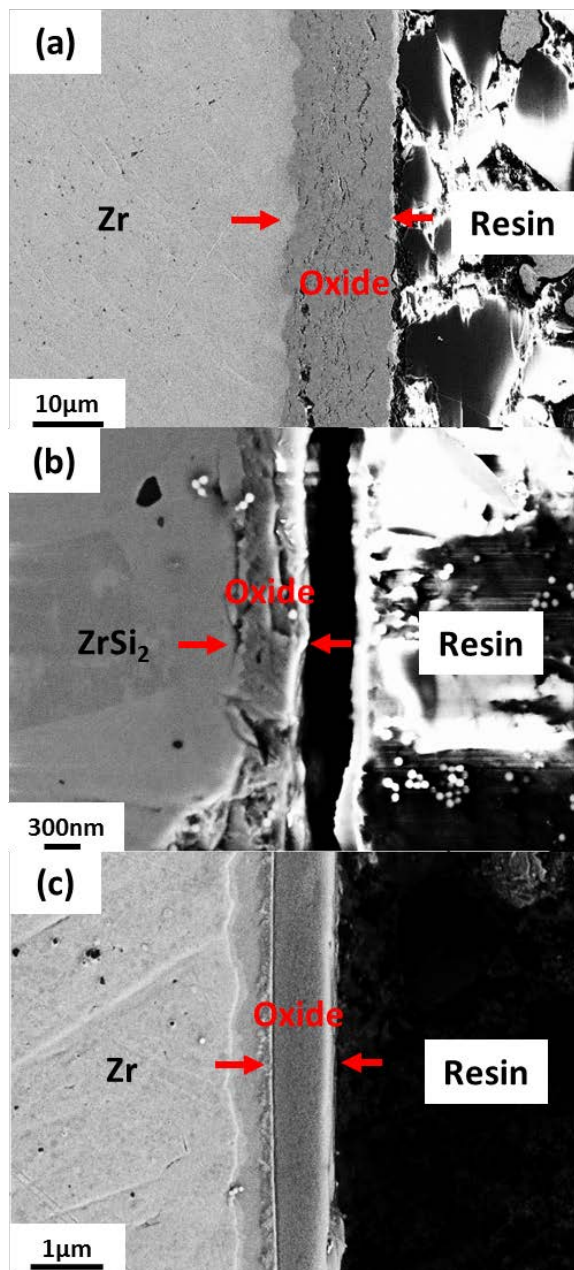


Fig. 3. SEM cross sectional images of (a) Zirc-4, (b) ZrSi_2 , and (c) PVD ZrSi_2 coating on Zirc-4 after 700 °C for 5 hours oxidation test at ambient air. Please make sure the scale bar in each image. The red arrows indicate oxide layer.

Pressurized Quench Test

The initial set of tests consisted of three quench experiments of the 316 stainless steel specimens performed at water in atmospheric saturation condition at nearly identical conditions. Figure 4 shows the test parameters and temperature history obtained for the same specimen. The temperature-

time curves reveal excellent repeatability of the test. The typical quenching curve introduces the general changes in boiling heat transfer regimes over time: film boiling, transition and nucleation boiling, natural convection. The temperature gradually decreases over time in the initial stage of quenching, where the stable vapor film covers the entire specimen surface (Figure 5a). As temperature of the surface decreases, the vapor film gets thinner and intermittent contact generating larger size bubble is observed (Figure 5b). Subsequently, the vapor film is destabilized at the bottom of the specimen and it propagates toward the top of the specimen, associated with transition from the film boiling to nucleate boiling regime (Figure 5c) with enhanced heat transfer coefficient. Therefore, the sudden temperature drop is observed in the quench curve. The vigorous bubble formation occurs on the surface in which the stable vapor disappears, and this refers to nucleate boiling regime (Figure 5d). Finally, natural convection regime is reached at the end of the quenching process (Figure 5e).

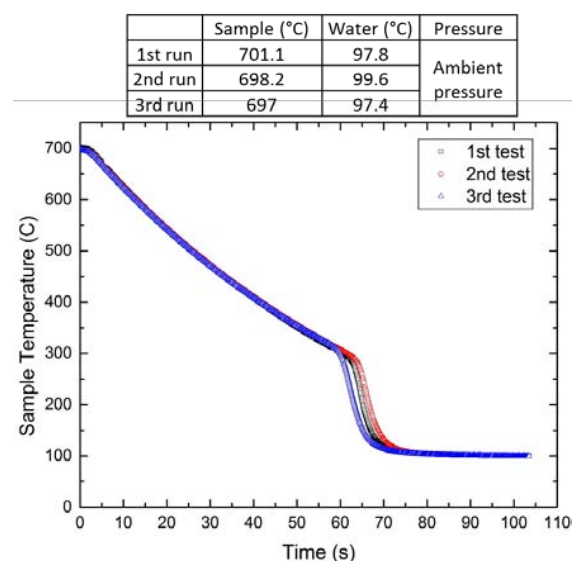


Fig. 4. Repeatability of quenching on bare 316 stainless steel specimen under saturated water in ambient pressure.

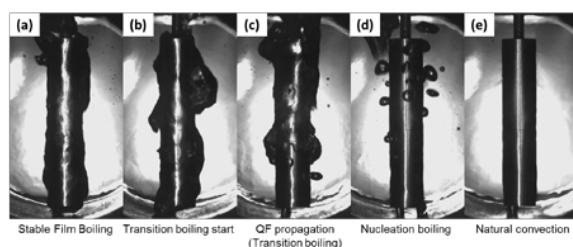


Fig. 5. High speed visualization (40 frames per second) of the 316 Stainless steel specimen during quenching at saturated water in ambient pressure, showing transition of boiling regime over time.

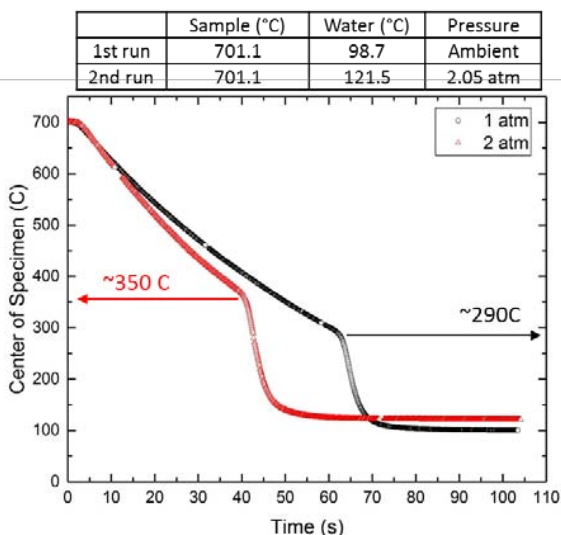


Fig. 6. Quenching curves with different system pressure.

Additionally, the quench test at 0.2 MPa (~2 atm) was performed using the 316 stainless steel specimen. The Figure 6 shows the experimental conditions and the quenching curve. The estimated minimum film boiling temperature increased with increasing system pressure, which is in good agreement with the published literature.⁸⁻¹⁰ Evaluation of the protective nature and boiling heat transfer of zirconium silicide coating on Zirc-4 specimen under the quenching process with elevated pressure will be performed and compared to uncoated Zirc-4 specimen.

CONCLUSIONS

Preliminary results supporting the use of Zr-silicide coating for enhanced accident tolerance of Zr-alloy fuel cladding under high temperature has been demonstrated. The high temperature oxidation behavior of bare Zircaloy-4, thin ZrSi₂ coating deposited on Zircaloy-4 substrate, and bulk ZrSi₂ were performed in air environment. The thin ZrSi₂ coating appeared to be an excellent barrier to oxygen diffusion so that oxidation of the underlying substrate was mitigated. To evaluate improved boiling heat transfer provided by the coating, the pressurized quench test facility has been designed and constructed. Preliminary tests using the 316 stainless steel rodlet under ambient pressure have been conducted to demonstrate the operability of the facility and initial scoping data was repeatable.

ACKNOWLEDGEMENTS

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Multi-Functional Zirconium-Silicide Coatings on Zirconium-alloy for Improved Accident Tolerance

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INTRODUCTION

Recently, development of protective coatings on zirconium-alloy (Zr-alloy) fuel cladding in light water reactors has been extensively investigated to enhance safety margins in accident scenarios. One accident scenario is degradation of the reactor core under a coolant-limited condition, where a large amount of Zr-alloy claddings would react with high temperature steam, leading to oxidation, hydrogen production, and loss of intrinsic mechanical properties of the fuel cladding. Although, total replacement of Zr-alloy with SiC-SiC_f composites or FeCrAl is being considered for the long-term, application of oxidation resistant coatings on zirconium-alloy is being investigated as a near-term solution to mitigate oxidation of Zr-alloy and increase the accident coping time. Coatings, such as chromium [1,2], Ti₂AlC [3,4], SiC [5], and Cr₃C₂-NiCr [6], deposited by various deposition techniques have been investigated. In addition, recent studies on modified heating surface for heat transfer enhancement provides basis on the optimal design of coated Zr-alloy claddings so that the new cladding can be achieve accident tolerance and heat transfer efficiency for both accident and normal operation conditions. Therefore, boiling heat transfer from the coated surface to water environment must be evaluated in parallel. In heat transfer performance, boiling heat transfer is characterized by nucleate boiling, critical heat flux (CHF), transition boiling, minimum film boiling temperature (T_{min}), and film boiling.

Zirconium-silicide (ZrSi₂) is a potentially attractive protective coating material for cladding applications. Although this material has not been studied extensively, it appears to be a promising candidate because of the high melting points [7], and the low neutron penalty [8], and the generally good oxidation resistance to transition metal silicides. It has been reported that oxidation of ZrSi₂ powder in a flowing air environment at elevated temperatures produced ZrO₂, SiO₂, and ZrSiO₄, pointing to the possibility of achieving highly protective surface layers of SiO₂ and ZrSiO₄ that would protect the material from further oxidation. [9] In this study, magnetron sputter deposition of ZrSi₂ on zirconium-alloy flats and cylindrical rods was performed. The coated samples were oxidized in high temperature air (700 °C, 1000 °C and 1200 °C) to evaluate their oxidation resistance. The coated

cylindrical rods were quenched in saturated water to observe transition boiling, T_{min} , film boiling regime, while the coated flats were tested in pool boiling facility to investigate nucleation boiling and CHF.

EXPERIMENTAL PROCEDURE**Materials**

Zirconium-silicide sputter targets (ZrSi₂) were procured from a commercial vendor. Test flat coupons of Zircaloy-4 (Zirc-4) substrates for deposition of zirconium-silicide coatings were prepared by grinding progressively with 320 grit and 600 grit SiC abrasive paper followed by cleaning with acetone and methanol. These samples were used for oxidation test and pool boiling tests.

For quench tests, a 300 mm-length Zirc-4 rod samples were procured from a commercial vendor, and were machined to short rodlets (50 mm-length and 10 mm-diameter) with 1.6 mm hole at the center of the rodlet to insert a thermocouple.

Coating Fabrication

Denton RF/DC Sputter system was used to fabricate ZrSi₂ coating on Zirc-4 flats and rodlets. In-situ plasma cleaning using Ar gas was performed prior to sputter deposition to remove any contamination and native oxide layer on samples surface. Coating parameters such as voltage bias, argon gas pressure, and deposition time were adjusted to get dense coating (~3 μm thickness).

Oxidation Tests

High temperature oxidation tests of the samples were performed in ambient air using commercial furnaces at the University of Wisconsin. The ZrSi₂ coatings were tested for oxidation at 700 °C for 20 hours, at 1000 °C for 1 hour, and 1200 °C for 10 minutes. After the exposure, the samples were air-cooled to room temperature. Oxide layer formation after the tests was characterized by optical and scanning electron microscopy (SEM).

Quench Tests

The quench test facility consisted of a heating zone, a water quenching chamber, and a pneumatic

actuator. The cylindrical Zirc-4 test section was heated to 700 °C in the heating zone and then plunged into the quench chamber with water in saturated condition using the air actuator. Pressure and temperature of the water in the quench was controllable, and temperature history and bubble generation during quench process were recorded. Details of this experimental system and procedure are explained in the previous work.[10] Four types of samples were prepared for the quench tests: bare Zirc-4, rough Zirc-4, smooth ZrSi_2 coated Zirc-4, and rough ZrSi_2 coated Zirc-4. Alumina sand blaster was utilized to fabricate the rough surfaces.

Pool Boiling Test

A schematic diagram of the pool boiling facility is shown in Fig. 1. The test flats are installed at the bottom of the pool and contacted with the heating block below. Thermal energy to the samples was generated by cartridge heaters inserted in the heating block. Temperature of the test surface was calculated from extrapolation of temperature measurements in the neck of the heating block. For this test, bare Zirc-4 flats and ZrSi_2 coated smooth Zirc-4 flats were used.

EXPERIMENTAL RESULTS

Oxidation Test

ZrSi_2 coatings (approximately 3.9 μm thickness) on Zirc-4 flats were oxidized at (i) 700 °C for 20 hours, (ii) 1000 °C for 1 hour, and (iii) 1200 °C for 10 minutes. The coated samples were pre-oxidized at 700 °C for 5 hours prior to the 1000 °C and 1200 °C tests to enhance oxidation resistance of the coating. The oxide layer thickness was measured by SEM cross-sectional images, which are shown in the Fig. 2.

The red arrows in Fig.2 indicate thickness of the oxide scales, and multi-layered nature of the oxide layer is also revealed in these figures. Oxide layer thickness for the ZrSi_2 coated Zirc-4 after 700 °C for 20 hours was 750 nm but the bare Zirc-4 at the same condition developed 65 μm thick oxide layer. This suggests an oxidation resistance improvement factor of the coating of more than 85 compared to bare Zirc-4 at 700 °C air. Moreover, after oxidation at 700 °C for 5 hours followed by the 1000 °C for 1 hour, total thickness of the oxide scale for the coated samples was about 7 μm , but that of the bare Zirc-4 oxidized under the same condition it was about 89 μm . The oxide layer thickness of the pre-oxidized coating after the 1200 °C test was about 20 μm , which was nearly one tenth of oxide scale thickness formed on the bare Zirc-4 (about 208 μm) under this condition. No spallation or cracks were observed on the ZrSi_2 coated samples arising from the rapid heating to high temperatures and cooling to room temperature. In short, oxygen permeation through the thin ZrSi_2 coating seems to be

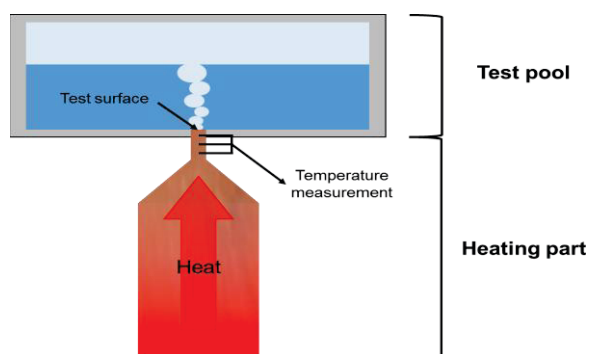


Fig. 2. Conceptual picture of pool boiling experiments.

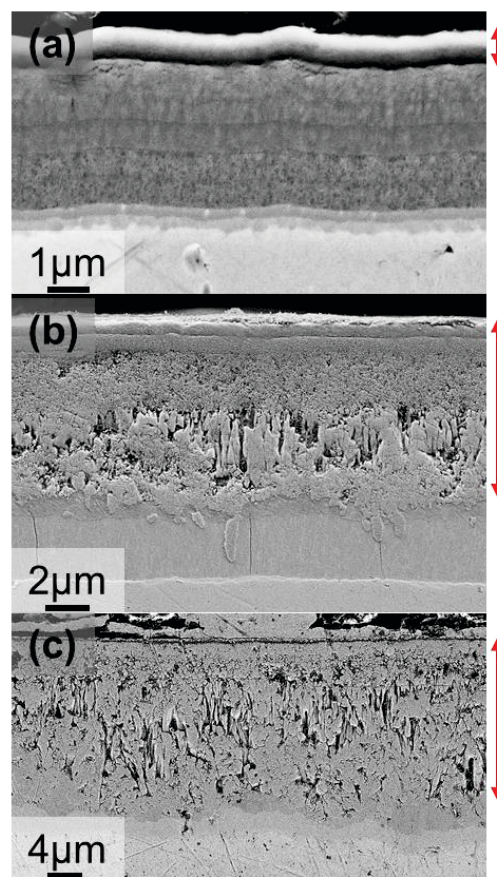


Fig. 1. SEM cross sectional images of (a) oxidized ZrSi_2 coating on Zirc-4 at 700 °C for 20 hours, (b) oxidized ZrSi_2 coating at 700 °C 5 hours followed by 1000 °C for 1 hour, and (c) oxidized ZrSi_2 coating on Zirc-4 at 700 °C for 5 hours followed by 1200 °C for 10 minutes at ambient air. The red arrows indicate oxide layer.

greatly reduced, indicating that the coating inherently is protective of the Zirc-4 under in high temperature air environment.

Quench Tests

The initial set of tests for bare Zirc-4 cylindrical rodlets was conducted to verify the repeatability and reproducibility of the experiment. Prior to the tests, deionized water ($18\text{M}\Omega$) was boiled in the quench chamber for 20 minutes to remove residual gas. The test specimen was heated up to 700°C and then plunged into the saturated water by the pneumatic actuator. Fig. 3 shows quench curves for three different bare Zirc-4 specimens under atmospheric condition. The center temperature vs. time curves show excellent reproducibility of the test. It was also observed that the three consecutive tests for a single specimen yielded very similar quench behavior. The inflection point after about 24 seconds in Fig. 3 represents the minimum film boiling temperature ($T_{\min}$), which represents a rapid transition from stable film boiling to nucleation boiling regime.

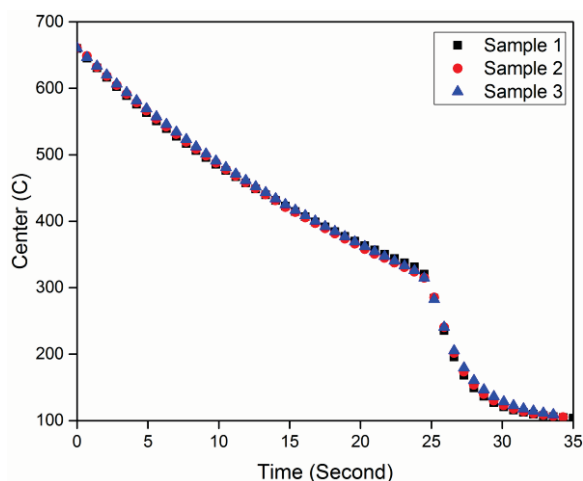


Fig. 3. Reproducibility of quench experiments on bare Zirc-4 sample performed in saturated water in ambient pressure.

Photographs of the cylindrical test sections after three consecutive quench tests are shown in Fig. 4. The average surface roughness (R_a) for bare Zirc-4 and smooth ZrSi_2 coated Zirc-4 was approximately $0.2\text{ }\mu\text{m}$ but that for the rough Zirc-4 and rough ZrSi_2 coated Zirc-4 was about $20\text{ }\mu\text{m}$. Without the ZrSi_2 coating, the Zirc-4 sample surface appeared to be heavily oxidized during the quench tests as suggested by dramatic change in surface color of the samples. In contrast, the coated samples revealed bluish color. No spallation of the coating was identified, indicating that the coatings withstood thermal stress during the rapid cooling process.

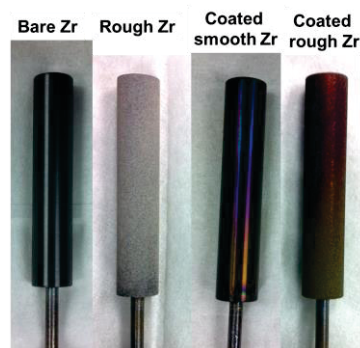


Fig. 4. Photograph of the quench test samples after three consecutive tests: bare Zirc-4, rough Zirc-4, smooth ZrSi_2 coated Zirc-4, and rough ZrSi_2 coated Zirc-4.

Center-line temperature histories of the different surface conditions are shown in Fig. 5. The inflection points for the coated samples were slightly higher than uncoated samples. Remarkable enhancement of boiling heat transfer was observed in the initial stage for the roughened surfaces, triggering early transition into nucleation boiling regime. Further studies will be performed to corroborate these results using bubble dynamics and estimation of surface temperature vs. heat flux during the quench process.

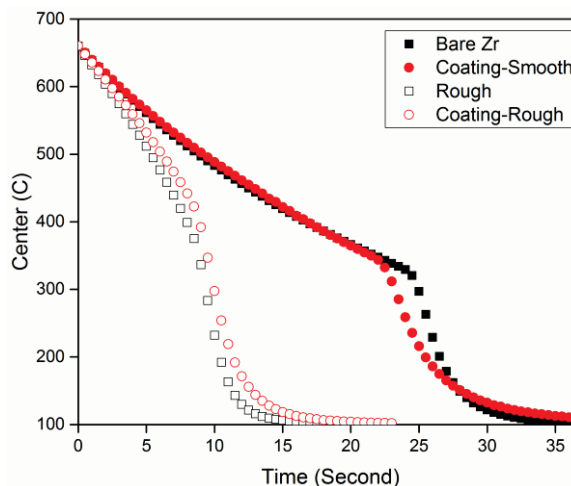


Fig. 5. Quench curves of bare Zirc-4, ZrSi_2 coated smooth Zirc-4, rough Zirc-4, and ZrSi_2 coated rough Zirc-4 at ambient pressure.

Pool Boiling Tests

Pool boiling experiment for bare Zirc-4 and ZrSi_2 coated Zirc-4 was carried out to determine the critical heat flux (CHF) for the various surface conditions. Test sample was connected with a heating block, which transferred thermal energy from cartridge heaters to the test sample, and boiling occurred at the

top surface of the test sample. All experiments were conducted for the saturated temperature condition at atmospheric pressure with deionized water. As shown in Fig. 6, higher CHF value (1 MW/m^2) was measured in the ZrSi_2 coated surface than bare Zirc-4 surface (770 kW/m^2). This means that the thin coating would provide an additional 30% margin when compared to the bare Zirc-4 cladding surface.

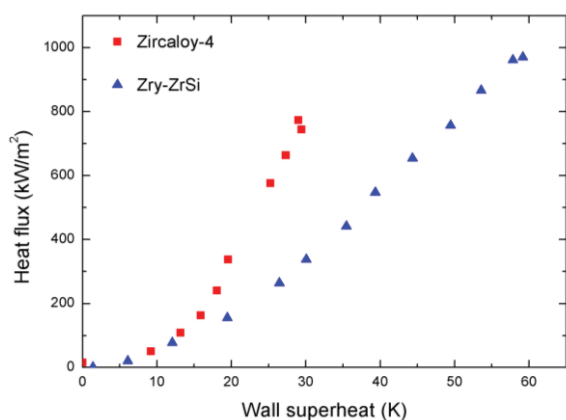


Fig. 6. Boiling curve of bare Zirc-4 and ZrSi_2 coated Zirc-4 used for CHF measurements

CONCLUSIONS

ZrSi_2 coatings deposited on Zirc-4 samples using the magnetron sputtering technique was shown to drastically mitigate oxidation in 700°C , 1000°C , and 1200°C air environments. The boiling heat transfer characteristics of Zirc-4 in roughened and coated surfaces were investigated using quench tests and pool boiling experiments. Preliminary tests indicate that ZrSi_2 coating increased minimum film boiling temperature slightly compared to bare Zircaloy-4 surface, but surface roughness had a more dominant effect in accelerating the cooling process. Pressure and subcooling effects on the quench process of the coated surfaces will be investigated. The pool boiling experiment showed that the coated surface provided 30% higher critical heat flux than uncoated surface. These preliminary results support the use of ZrSi_2 coating on Zr-alloy to enhance accident tolerance of the Zr-alloy fuel cladding in LWR.

ACKNOWLEDGEMENTS

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Preliminary Evaluation of Anodic Oxidation and Electrophoretic Deposition for Heat Transfer Enhancement in Accident Tolerant Fuel Cladding

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ABSTRACT: Cladding embrittlement of zirconium-based alloys under accident conditions becomes potential threats to the environment and public due to radioactive material release in nuclear power plants. This issue has motivated research on the development of new cladding materials to tolerate nuclear fuel cladding from accidents. A short-term approach is to deposit protective, oxidation resistant coatings on the Zr-alloy cladding to improve corrosion resistance and reduce hydrogen pickup.

In conjunction with the material development, Accident Tolerant Fuel (ATF) claddings should also have enhanced heat transfer performance under normal operations and accident conditions.

In this paper, we utilized anodic oxidation (AO) and electrophoretic deposition (EPD) to enhance heat transfer performance of the cladding. The preliminary studies on boiling heat transfer characteristics of the cladding material with micro/nano structures fabricated by AO on bulk ZrSi₂ and EPD of ZrSi₂ particles on Zircaloy-4 are reported. Under the oxidation test at 700 °C, EDS and weight gain data showed anodically oxidized ZrSi₂ has comparable or even superior oxidation resistance compared to bulk ZrSi₂. As a preliminary assessment of heat transfer characteristics, the wettability of the surfaces was quantified using liquid spreading speed and the contact angle as metrics to determine optimal process parameters to enhance heat transfer. EPD samples showed the best wettability under the applied voltage of 200 V attributed to sufficient deposition or relatively uniform deposition compared to 100 V or 600 V. Initial results of boiling heat transfer (BHT) of ZrSi₂ coated Zircaloy-4 in pool boiling also showed 29% increased critical heat flux (CHF) compared to the Zircaloy-4 surface without coating.

KEYWORDS: BHT, CHF, Micro/Nano Surface Modification, Wettability, Accident Tolerant Fuel Cladding, ZrSi₂

I. INTRODUCTION

For more than a half decade, zirconium-alloy has been widely used for cladding materials and fuel bundle structures largely due to its low neutron absorption and desirable mechanical strength (Ref. 1). In contrast to these remarkable properties, zirconium based alloys are susceptible to oxygen dissolution and hydride precipitation (Ref. 1). Under loss-of coolant accidents (LOCAs), zirconium undergoes ductility loss due to oxide phase formation which accelerates oxidation rate at temperatures above 1200 °C. At even higher fuel burnup, cladding embrittlement deteriorates by hydrogen atom precipitation mainly as a result of the waterside cladding corrosion.

As cladding oxidation plays a key role in cladding embrittlement, there has been great interest in replacement of current zirconium based cladding with accident tolerant fuel (ATF) claddings to improve the safety of LWRs and various potential targets have been discussed. There are many candidates of ATFs and one possible approach is to replace the current cladding material to other accident tolerant materials such as the advanced steel or SiC/SiC-composite. However, this concept is in a

premature stage of development and it requires major modifications of nuclear core designs. For a near term approach, coating on zirconium alloys is readily applicable without a significant change in operational characteristics (Ref. 2). In parallel to ATF development, heat transfer characteristics of cladding should be evaluated to maintain the core coolability (Ref. 3). Heat transfer performance during phase-change is necessary as material has different thermal properties with phase-change, however, the research on ATF regarding heat transfer has been far limited due to early R&D status of ATF.

In this regard, Pohang University of Science and Technology (POSTECH) launched a collaborative project called I-NERI supported by the National Research Foundation of Korea with University of Wisconsin-Madison (UW-Madison) in USA to develop an ATF cladding technology based on zirconium silicide (ZS) coated on conventional Zircaloy-4 cladding. ZS possesses self-healing effects, the ability to fill the cracks and recovery the strength in the form of SiO_2 and ZrSiO_4 (Ref. 4) which can significantly minimize the outcomes in design-based accidents (DBA). For an optimal design of cladding, heat transfer performance of ZS coating should be evaluated by boiling heat transfer (BHT) and critical heat flux (CHF). BHT and CHF represent the efficiency of heat removal and upper limit of operational heat flux, respectively. BHT of claddings shows the cladding's heat transfer efficiency under normal operations or DBAs and CHF is related to the safety margin of nuclear reactor. CHF enhancement can tolerate additional heat generation in DBAs and this can be achieved by increasing wettability of the claddings (Ref. 5). The goal of this I-NERI project is to enhance heat transfer performance of the cladding and accident tolerant characteristics by engineering micro/nano structures on the ZS coating surfaces. UW-Madison has developed ZS PVD (Physical Vapor Deposition) coating on zircaloy substrate and played a key role in evaluation of its accident tolerant characteristics. POSTECH has performed fabrication of ZS micro/nano structures and preliminarily assessed heat transfer on ZS PVD coated zircaloy-4.

In this paper, the preliminary studies on boiling heat transfer characteristics of the cladding material with two surface modifications are reported. Micro/nano structures were fabricated by anodic oxidation (AO) on bulk ZrSi_2 and electrophoretic deposition (EPD) of ZrSi_2 particles on Zircaloy-4. The modified surfaces were evaluated and the compositions and micro/nano structures of each sample were characterized by XRD, EDS and SEM. The oxidation resistance was measured by calculating the cumulative weight gain at three different isothermal oxidation tests.

II. EXPERIMENT

II.A. Micro/nano structure fabrication and PVD coating

II.A.1. ZrSi_2 PVD coating on zircaloy-4

Physical Vapor Deposition (PVD) is used for deposition of ZrSi_2 coating on flat zircaloy-4 samples. PVD refers to deposition process under vacuum condition where coating materials are sputtered out from the target and condensed on the substrate forming a coating (Ref. 6). Prior to the deposition, all zircaloy-4 substrates (10 mm x 10 mm x 0.88 mm) were ground by 220, 1200 and 2000 grit SiC papers in sequence and ultrasonically cleaned in acetone and ethanol bath for 10 minutes, respectively. Grinding procedures were kept the same for all following surface fabrication processes. More detailed procedures of PVD process are presented in Ref. 3. The power and pressure were 135 W and 4mTorr (Ref. 7).

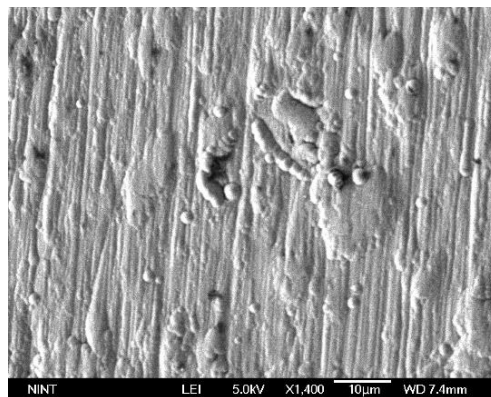


Fig. 1. SEM image of ZrSi_2 PVD coated zircaloy-4.

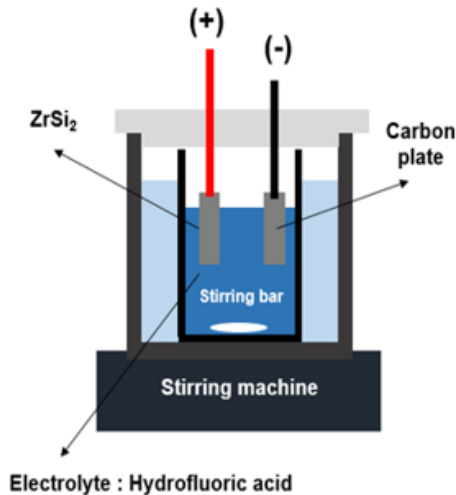
II.A.2. Anodic Oxidation (AO)

Anodic oxidation was used to create microscale and nanoscale structures on zircaloy-4 surface. Anodic oxidation is an electrochemical fabrication process where electric potential is used to accelerate chemical reactions at the interface between the metal and a counter electrode. Fig. 2 (a) shows the experimental setup for anodic oxidation and hydrofluoric acid solution was used as the electrolyte with concentration varying from 0.5 ~ 2 wt%. Temperature was maintained to be 10 °C during the reaction. Parameters affecting the reaction include the current density, applied voltage, acid strength and exposure time and these can be varied to obtain microstructures with different morphologies and thickness. Current density is related to the reaction rate and this can be accelerated by increasing applied voltage. The samples were baked out at 150 °C in an electric furnace to remove remaining chemical components.

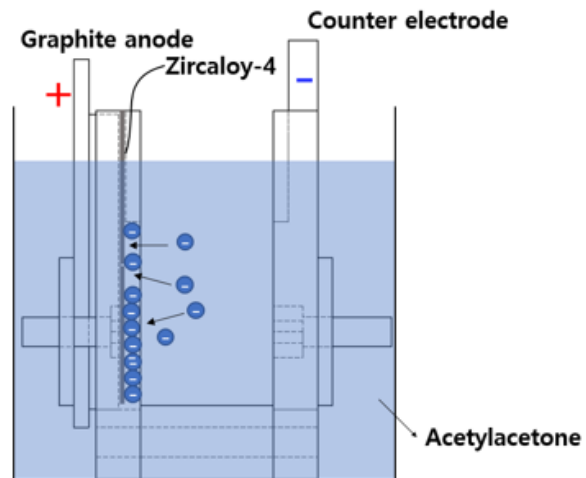
II.A.3. Electrophoretic deposition (EPD)

Electrophoretic deposition is a deposition of particles in a suspension to a substrate in an influence of an electric field (Ref. 12). This process can be applied to ceramic and metallic compounds and to easily create porous structures with a simple schematic, regardless of geometries, especially on round structures such as fuel rods. Porous structures can increase liquid inflow rate by increasing permeability and liquid inflow rate is directly related to CHF enhancement (Ref. 8 and 9). Parameters affecting the EPD can be classified into suspension parameters and process parameters. Liquid inflow rate in porous media can be improved by increasing porosity and capillary pressure, so these two factors were optimized by changing as-mentioned parameters.

To increase permeability of the deposit, particles with the mean diameter of 44 μm (size distribution shown in Fig. 3) were selected in this study, unlike previous studies which mainly utilized nanosized particles (Ref. 10). Process parameters include process time, applied voltage and particle concentration. The concentration of solid suspension was maintained at 0.5 wt % for all depositions as more porous structures are generated from suspensions with lower concentrations. Before deposition, particles were ultrasonically stirred for 2 hours. Applied voltages had been varied from 100 to 600 V to acquire particles with different porosity and mean particle sizes (Ref. 11). After deposition, samples were sintered in the furnace at 200 °C or 400 °C for 2 hours to acquire sufficient interfacial strength between the deposit and substrate.



(a) Anodic oxidation



(b) Electrophoretic deposition

Fig. 2. Schematic of (a) AO and (b) EPD.

II.B. Oxidation tests

Isothermal oxidation tests were performed at temperatures of 700, 1000 and 1200 °C in stagnant air condition. Air oxidation tests at 1000 and 1200 °C were performed only for 10 minutes as the samples were rapidly oxidized. Oxidation tests were performed on bare zircaloy-4 substrate, EPD coated zircaloy-4, bulk ZrSi_2 and anodically oxidized ZrSi_2 . Additionally, oxidation resistance of FeCrAl was evaluated to compare with ZS. At 700 °C, the oxidation time was varied from 1 hour to 24 hours to compare the oxidation kinetics of each sample. Weight of the samples were measured using a balance (Entris, Satorius).

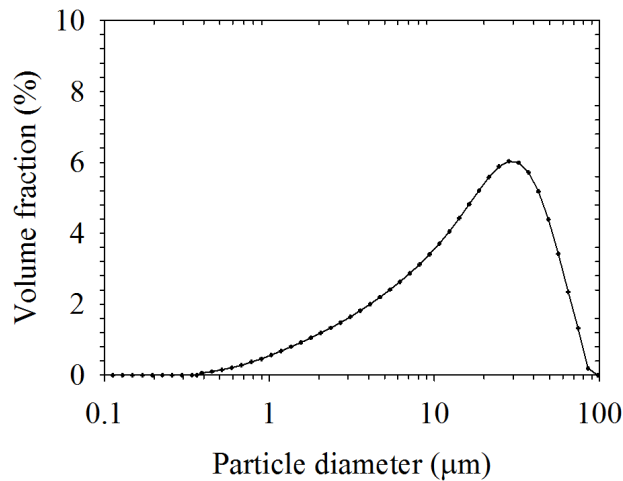


Fig. 3. Particle size distribution of ZrSi_2 for EPD.

II.C. Thermohydraulic experiment

II.C.1. Liquid spreading speed measurement

The wettability of the surface can be characterized by the displacement of triple line (TL) over time. 40 μl of water droplet was dropped on the top and the droplet's movement was observed (Fig. 4). The displacement of TL was calculated by subtracting the average radius of the previously wetted area from that of currently wetted area with a time interval of 1 second.

II.C.2. Pool boiling experiment on ZS PVD coating

Pool boiling was conducted on ZrSi_2 coated zircaloy-4 surface. Zircaloy-4 substrates were cut to a disk with diameter and thickness of 10 mm and 1.5 mm, respectively. All samples were drilled to the center to insert thermocouple (0.5 mm diameter, K type, omega). Heat was transferred to the samples from heated cartridge heaters by conduction and boiling occurred on the top of the surface. All experiments were performed under saturated condition at atmospheric pressure of DI water. The schematic of pool boiling is shown in Fig. 5. Applied heat flux was calculated from temperature measurements at the sample. Surface temperature was estimated using Fourier's law by extrapolating temperature measured by thermocouple. Heat flux was calculated by measuring the temperatures at three different points in the heat block and applying Fourier's law.

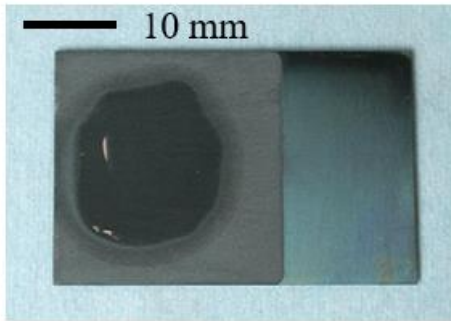
III. Results and discussion

III. A. Oxidation tests

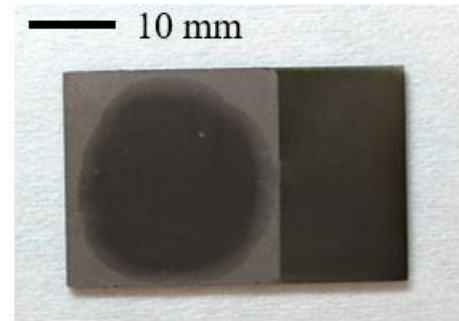
Weight gain data of each specimen is shown in Table 1. For an isothermal oxidation test at 700 °C, The weight gain and oxidation time is plotted in Fig. 7 to compare oxidation kinetics of different specimens. The overall trend of weight gain follows the following equation.

$$\frac{\Delta m}{S} = k_m \cdot t^n \quad (1)$$

Δm is the increased weight after oxidation (mg), S refers to the sample surface area (m^2), k_m is the rate constant and t is the oxidation time (s). When n approaches to $1/2$, it is applicable for a protective oxide scale. In this regime, the weight change is mainly due to diffusion of oxygen in oxide layer. When cladding is more resistant to oxidation, the exponent is equal to or less than $1/3$. When oxide scale loses protective characteristics, oxygen transportation across the layer can be accelerated through cracks and n can be linear ($n=1$) or even higher (Ref. 12). Mass change of bare zircaloy-4 shows an exponent greater than 1 after 5 hours, indicating that it does not resist oxygen penetration. Almost the same phenomenon is shown in EPD coated zircaloy-4. The overall trend of $ZrSi_2$ and AO $ZrSi_2$ had n lie between $1/2$ and $1/3$. However, all weight gain data were less in AO $ZrSi_2$ than in bulk $ZrSi_2$ probably due to the pre-oxidized outer layer. FeCrAl maintained its mass after 5 hours, indicating protective Al_2O_3 formation (Ref. 13). After oxidation at $1000^\circ C$, the zircaloy-4 surfaces formed various cracks, however, no visible cracks can be seen on the surface of bulk $ZrSi_2$ and FeCrAl (Fig. 7).

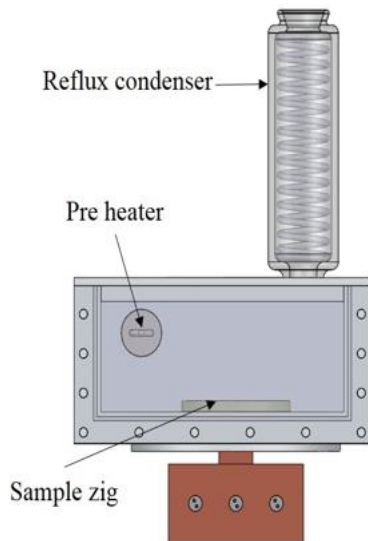


(a) Applied voltage: 100 V

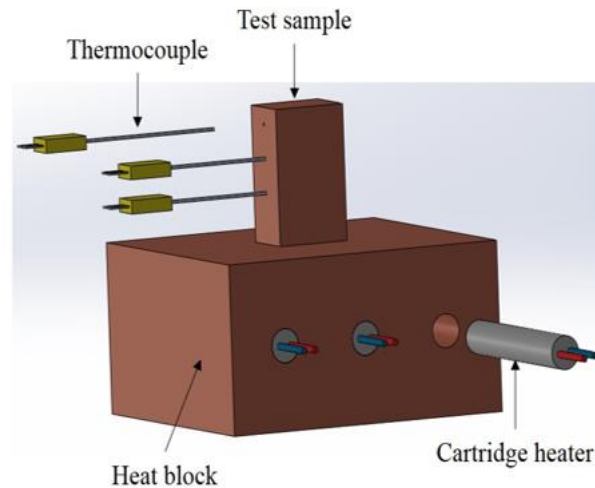


(b) Applied voltage: 200 V

Fig. 4. Droplet spreading after 6 seconds on EPD samples deposited at (a) 100 V and (b) 200 V.



(a) Pool boiling experimental loop.



(b) Conductive heating block.

Fig. 5. Experimental setup for pool boiling. (a) Pool boiling experimental loop. (b) Conductive heating block.

TABLE I. Weight gain ($\times 10^3 \text{ mg/m}^2$) of different cladding materials

Temperature and duration	Zircaloy-4	EPD coating on Zircaloy-4	ZrSi ₂ bulk	AO ZrSi ₂	FeCrAl
700 °C, 1 hour	8.077	3.462	0.934	0.329	1.960
700 °C, 5 hours	16.184	-	-	-	0.225
700 °C, 10 hours	42.692	39.615	3.738	1.647	0.490
700 °C, 24 hours	113.077	114.231	2.804	-	0.490
1000 °C, 10 min	155.878	-	-	-	0.068
1200 °C, 10 min	-	-	-	-	1.040

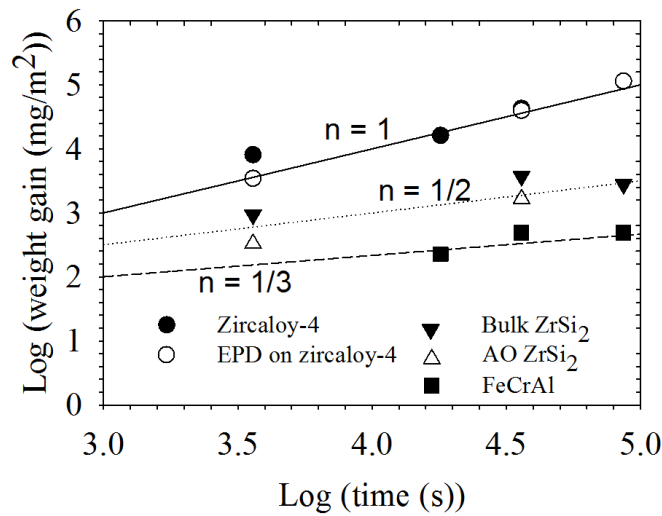


Fig. 6. Mass change of zircaloy-4 and ATF candidates over time at 700 °C in log-log scale.

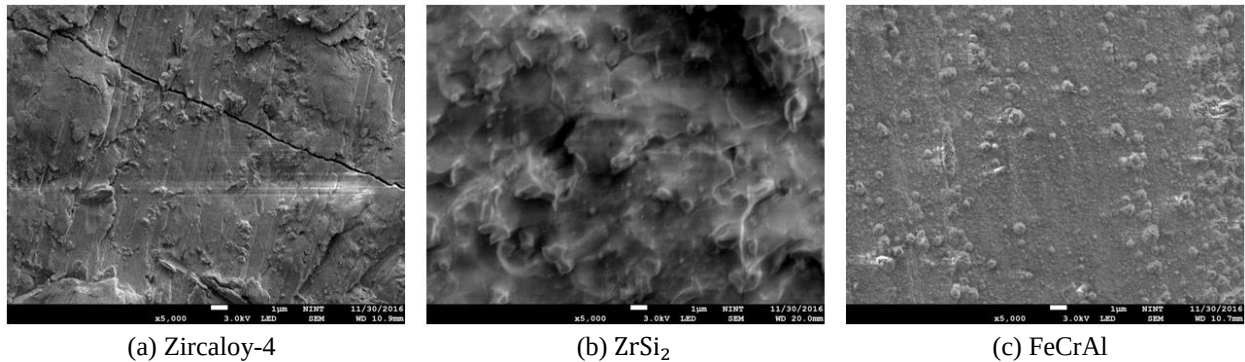


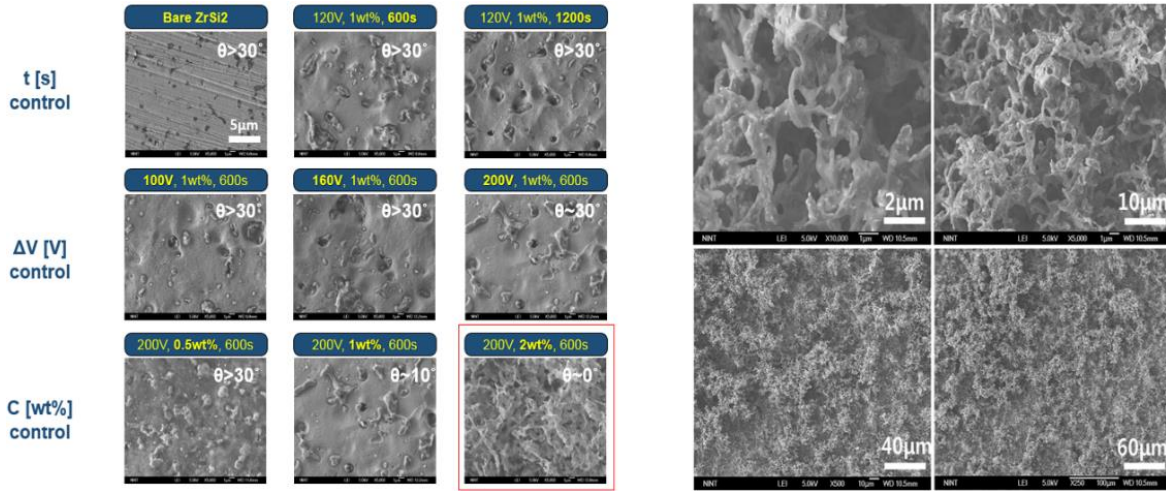
Fig. 7. SEM images of zircaloy-4 and ATF cladding candidates after 1000 °C isothermal oxidation test.

III. B. Thermohydraulic characteristics

III.B.1. Wettability of AO and EPD samples

As seen in Fig. 8 (a), the samples exposed to acid concentration of 2 wt% for 600 s showed the lowest contact angle. Wettability greatly changed with the increase of acid concentration due to the formation of various rough microstructures. More

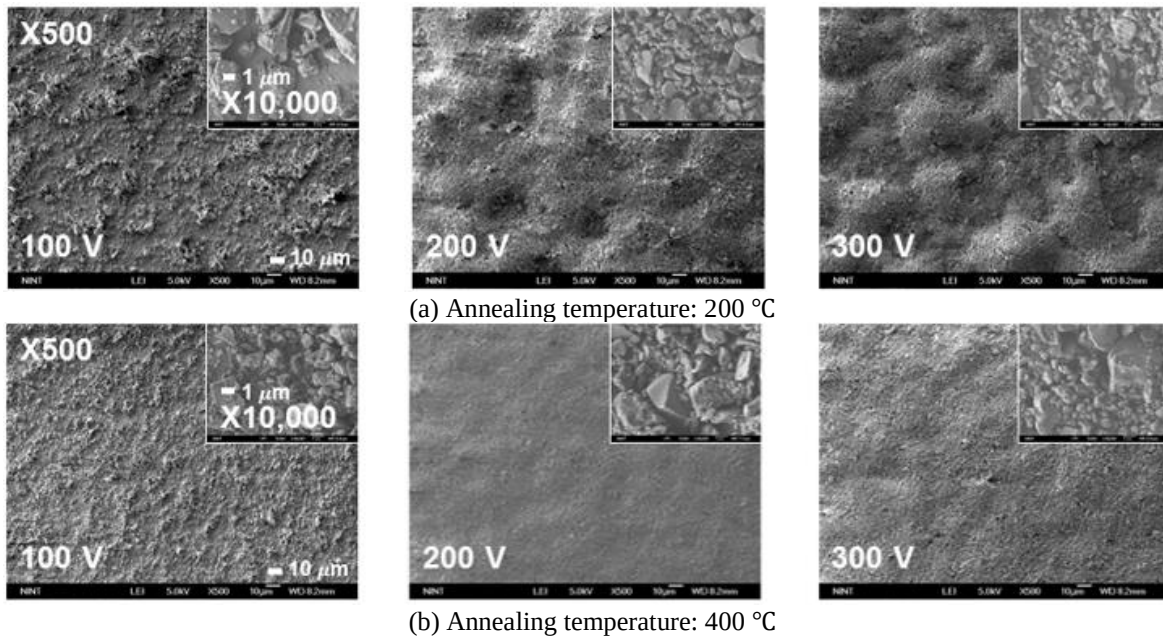
detailed SEM images of AO sample processed for 600 s in 2 wt% acid solution showed microstructures with branches of sub-microstructures as shown in Fig. 8 (b). In previous research (Ref. 14), liquid spreading was the main mechanism in CHF enhancement and CHF was greatly enhanced on superhydrophilic surfaces in pool boiling. The combination of nanostructures and microstructures created the highest enhancement of liquid spreading ability according to the previous study (Ref. 15). Accordingly, we concluded that the acid concentration will be the most dominant parameter in CHF enhancement due to micro/nano structures.



(a) SEM images of AO surfaces under different conditions.

(b) SEM images of AO with contact angle of 0°

Fig. 8. Anodically oxidized surface of ZrSi_2 . (a) Effects of exposure time, voltage and acid concentration. (b) Detailed SEM images of 200 V, 2 wt%, 600 s case.



(a) Annealing temperature: 200 °C

(b) Annealing temperature: 400 °C

Fig. 9. SEM images of EPD samples deposited at different voltages and annealed at (a) 200 °C and (b) 400 °C

Porous structures of EPD samples were characterized by SEM. TL displacements of EPD samples were plotted in Fig. 10. Surfaces of EPD samples have been flattened in higher sintering temperature because in EPD (Fig. 9 (a) and (b)), post-processing removes porosity to increase uniformity inside the deposit. This resulted in more apparent degradation of spreading speed in higher annealing condition easily seen by comparing Fig. 10 (a) and (b). Packed structures can collapse easily as void fraction is larger when the deposition is performed at higher voltages. At lowest voltage, the deposition was not sufficient and most part was not properly deposited. This resulted in the pinning of droplet after 6 seconds (Fig. 4 (a)). 200 V showed the highest or second highest spreading speed in both annealing conditions.

III.B.2. Pool boiling experiment on ZrSi_2 PVD coating

The results of pool boiling experiments on the plane zircaloy-4 sample and the ZrSi_2 coated samples are shown in Fig. 11. The wall superheat refers to the difference between wall temperature and saturated temperature. The slope in boiling curve is heat transfer coefficient and related to coolability of the surface. The peak value of the curve is the critical heat flux, the operational limit of heat flux input. Zircaloy-4 had higher heat transfer coefficient, which is expected as ZrSi_2 coating can provide thermal resistance. CHF was enhanced by 29 % when ZrSi_2 coating was applied on zircaloy-4. The higher CHF value can be explained by the increase of roughness due to the micro-sized bulbous structures shown in ZrSi_2 PVD (Fig. 1).

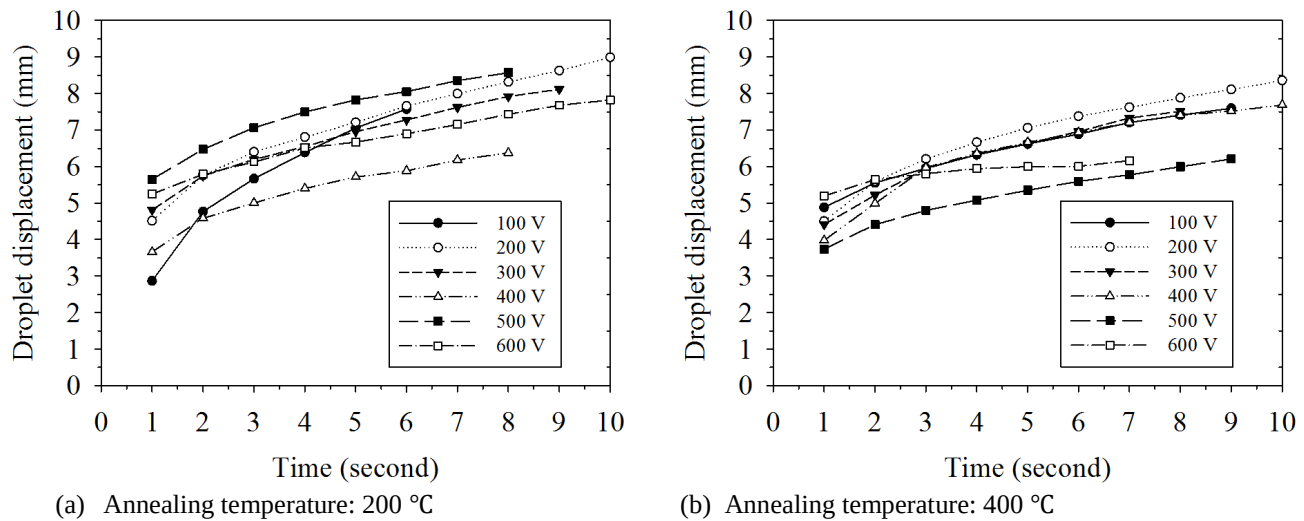


Fig. 10. Effect of annealing and applied voltages on spreading speed (a) Annealed at 200 °C. (b) Annealed at 400 °C.

IV. CONCLUSIONS

In this study, we tested two micro/nano structure fabrication methods to develop thermally enhanced ATF cladding. AO and EPD were optimized on bulk ZrSi_2 and zircaloy-4, respectively. Oxidation resistance of ZrSi_2 was verified by performing isothermal oxidation tests and the oxidation results of various candidate ATF candidates were compared. Pool boiling experiment was performed on zircaloy-4 surface with ZS PVD coating to investigate the feasibility and boiling performance of ZS coating. The following conclusions were made in this work.

- 1) ZrSi_2 has negligible weight gain unlike zircaloy-4 in the isothermal oxidation test at 700 °C.
- 2) FeCrAl showed the least weight gain in 700 °C oxidation test.
- 3) Spreading occurred in AO when processed in solution with acid concentration of 2 wt% and EPD has the optimal applied voltage.
- 4) EPD coating cannot improve oxidation resistance due to oxygen penetration through porous structures and combination with ZrSi_2 PVD coating will be made in the further study.

- 5) ZS PVD coating without micro/nano structure fabrications improved CHF by 29 %.

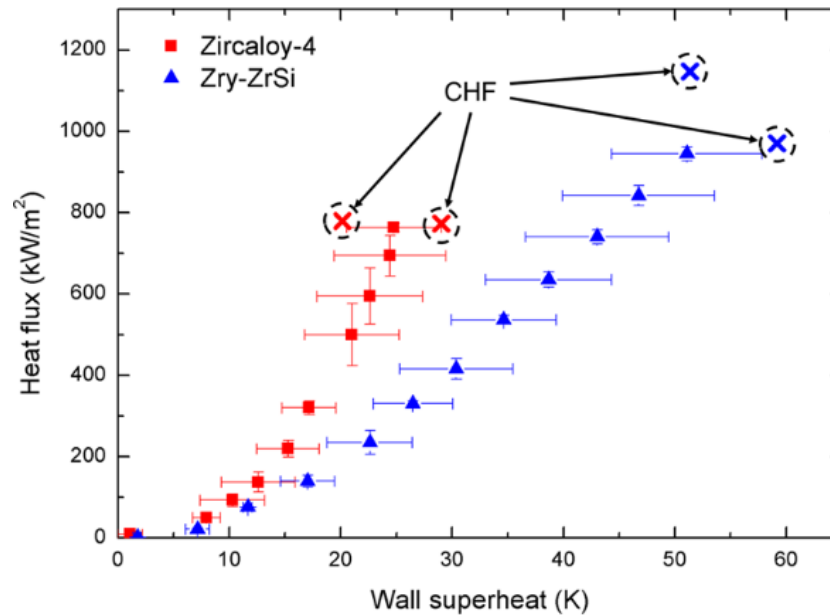


Fig. 11. Pool boiling experiments on zircaloy-4 and ZrSi₂

The results of the air oxidation test show ZrSi₂ PVD coating enhanced oxidation resistance of zircaloy-4 and its mass gain over time showed oxidation resistant behavior. The boiling curves show PVD coating can improve CHF on top of oxidation resistance, therefore, CHF will be further improved with micro/nano structures which is the main goal of this I-NERI project. The wettability of AO and EPD was optimized and these two methods will be applied on PVD coating to improve CHF in the next study. Application of these fabrication methods to the cladding requires the structural and mechanical improvements. The thickness of AO should be lower than PVD coating thickness to maintain oxidation resistance and EPD needs sufficient adhesion to maintain porous structures in water flow. Thickness control of AO and adhesion tests of EPD will be handled in the following study as well.

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