

4.17 Metallic and Ceramic Coatings for Enhanced Accident Tolerant Fuel Cladding

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Abbreviations

ATF	accident tolerant fuel	LOCA	loss of coolant accident
BDBA	beyond design basis accident	LTRs	lead test rods
BWR	boiling water reactor	LWRs	light water reactors
CVD	chemical vapor deposition	NCD	nanocrystalline diamond
DLI-MOCVD	direct liquid injection of metal organic precursors CVD	NWC	normal water chemistry
DPA	displacements-per-atom	PCMI	pellet-clad mechanical interaction
HEA	high entropy alloys	PE-CVD	plasma-enhanced CVD
HVOF	high velocity oxygen fuel spraying	PVD	physical vapor deposition
HWC	hydrogen water chemistry	SHE	standard hydrogen electrode
		TMN	transition metal nitride
		WWER	water-water energetic reactor

4.17.1 Introduction

Zirconium-based alloys, which were selected and developed as replacements for components made of stainless steel in the 1950s, feature multiple desirable performances, e.g., low thermal neutron absorption cross section, adequate hydrothermal corrosion resistance and good mechanical properties under neutron irradiation, as fuel claddings for light water reactors (LWRs) during steady-state normal operations.^{1,2} Advanced nuclear grade zirconium-based alloys, like M5® from Framatome and ZIRLO™ from Westinghouse, exhibiting optimized performances under normal conditions have been deployed via decades of intensive investigation and development and have resulted into exceptionally low failure rates.³ However, during typical loss of coolant accident (LOCA) or beyond design basis accident (BDBA) scenarios the residual decay heat can lead to rapid core temperature increase and the performance of Zr-alloy fuel claddings are thus highly challenged.⁴ One inherent limitation of zirconium-based alloys during accidental scenarios, namely the rapid exothermic zirconium-steam oxidation reaction accompanied by strong heat and hydrogen

release, cannot be prevented via optimizing their chemical compositions and/or manufacturing processes.⁵ At temperatures beyond 1200°C, the chemical heat release due to the exothermic Zr-steam reaction may exceed the residual decay heat and thus strongly affect the accident progression.⁴ The released hydrogen results in the risk of detonation when exposed to oxygen/air. In addition, zirconium alloy claddings can absorb significant amounts of hydrogen during both normal and accident conditions. Hydrogen can dissolve or precipitate as brittle hydrides in the matrix. Hydrogen embrittlement dramatically degrades the mechanical performance of zirconium alloy claddings, limiting fuel burnup under normal operations and challenging the physical integrity of the cladding tube especially during accident conditions.⁶

The Fukushima Daiichi Accidents in 2011 highlighted the detrimental performance characteristics of the zirconium-based alloy fuel claddings during (severe) accidental scenarios and the need to develop advanced accident tolerant fuel (ATF) claddings for enhancing the safety margins of water-cooled reactors.⁷ Advanced ATF materials should tolerate the loss of active cooling inside the core for a considerably longer period of time and up to higher temperatures (> 1200°C) relative to the standard UO₂/Zr-alloy clad fuel system offering additional coping time for severe accident management. In the meantime, they must demonstrate the potential for maintaining or improving fuel performance during normal operating conditions.⁸ A variety of ATF cladding concepts have been proposed and evaluated worldwide.^{7–11} One approach is to replace the state-of-the-art Zr-based alloy cladding with new materials exhibiting much lower steam oxidation kinetics resulting in less heat and hydrogen production. This approach comprises mainly three types of materials, namely FeCrAl-based alloys,¹² lined Mo-alloy cladding¹³ and SiC/SiC composites.¹⁴ These potential accident-tolerant cladding alternatives using novel materials remain a long-term solution that may require substantial redesign of the reactor core. Another more near-term evolutionary strategy can be surface modification of the zirconium-based alloy cladding with an innovative high-temperature oxidation/corrosion resistant metallic or ceramic coating.¹⁰ This solution, assuming thin coatings, represents an incremental change to the current UO₂ fuel/Zr-alloy clad structures and allows easier licensing.

Decorative and functional coatings have seen numerous applications in a wide range of engineering systems; some recognizable examples include photochromic coatings, hard nitride coatings and thermal barrier coatings, etc. A variety of processes are also commercially available to fabricate the coatings.¹⁵ Depending on the coating applications, one or often multiple primary functional properties are required. The extremely harsh environments inside the nuclear core obviously demand robust coatings that can fulfill stringent performance requirements and technical specifications.¹⁶ An ideal ATF coating or coated Zr-alloy cladding is foreseen to meet the following unique requirements:^{10,11}

- Reduced hydrothermal corrosion rate and stored hydrogen inventory during normal operations;
- High adherence and ductility to sustain a high level of deformation and stress (for instance, irradiation induced swelling and creep, pellet-clad mechanical interaction [PCMI], clad ballooning);
- Chemical and mechanical compatibility with the Zr-alloy cladding substrate during normal and off-normal conditions;
- Significantly reduced oxidation kinetics in high-temperature steam/air atmosphere and higher mechanical strength leading to increased coping time relative to bare Zr-alloy cladding during accident scenarios;
- Adequate coating thickness to provide enhanced accident tolerance as well as negligible impact on fuel performances (including neutron economy, fuel temperature, critical heat flux, etc.) within the core;
- Capability to coat full-length cladding tube at low temperature (< 500°C) with excellent process stability and reproducibility.

The two basic yet prerequisite requirements of materials considered as coatings for enhanced ATF cladding applications are their resistance to hydrothermal corrosion (normal operations) and to high-temperature steam/air oxidation (accidental scenarios). Both working environments demand the growth of a thermodynamically stable, adherent oxide layer on the surface that acts as an effective diffusion barrier.⁷ Development and validation of various proposed coating concepts to date mainly focus on determining their protective capability under one or both regimes simulating out-of-pile conditions. This article reviews current research and development status of numerous metallic and ceramic coating concepts on Zr alloys for enhanced ATF cladding.

4.17.2 Principal Coating Concepts

The majority of studies on surface modification of Zr-based alloys was initiated after the Fukushima accidents; the few studies prior to Fukushima focused on improving their hydrothermal corrosion resistance to withstand higher burnup^{17,18} and alleviating

Table 1 Summary of different types of proposed coating materials on Zr alloys as coated ATF claddings

Metallic coatings	Single element	Al, Si, Cr
	Intermetallic/alloy	Zr-Si, Cr-Al, CrAlSi, FeCrAl, AlCrMoNbZr (HEA)
Ceramic coatings	Oxide	Al ₂ O ₃ , Cr ₂ O ₃ , ZrO ₂
	Carbide	C (CVD diamond), SiC, CrC, ZrAlC
	Nitride	TiN, CrN, TiAlN, CrAlN, CrAl(Si/Ti)N
	MAX phase	Ti ₂ AlC, Cr ₂ AlC, V ₂ AlC
Multilayer coatings	Ti/TiN, Cr/CrN, Al/Al ₂ O ₃ , Cr/CrAl, Mo/FeCrAl, ZrO ₂ /FeCrAl, TiC/Ti ₂ AlC, ZrSi ₂ /Zr ₂ Si, TiN/TiAlN, AlCrMoNbZr/(AlCrMoNbZr)N	

Note: Si and C (CVD diamond) are classified as metallic and carbide here for simplicity.

Table 2 Summary of selected physiochemical properties of principal coating materials

	Density (g/cm ³)	Melting/solidus temperature (°C)	Thermal expansion coefficient ($\times 10^{-6} K^{-1}$, RT)	Thermal conductivity (W/(m K), RT)
Zircaloy-4	6.56	1850	6.0	21.5
Al	2.70	660	23.2	237
Si	2.33	1410	2.6	148
Cr	7.14	1850	6.7	93.7
Mo (barrier)	10.28	2623	4.8	138
ZrSi ₂	4.88	1620	~30	–
FeCrAl (Kanthal APM)	7.10	1500	11.0	11
HEA (AlCoCrFeNi)	~6.50	~1300	12–16.5	10–22
Al ₂ O ₃	3.96	2044	8.1	~18
Cr ₂ O ₃	5.22	2330	7.1	~12
ZrO ₂	5.68	2715	7.0 (monoclinic) 12.0 (tetragonal)	1.67 (monoclinic)
CVD diamond	2.26	3650 (sublimation)	~1.0	>120
3C-SiC	3.10	2830 (decomposition)	~4.4	>140
Cr ₇ C ₃	6.5–7.0	~1765	–	–
TiN (TiAlN) coating	5.22	2930	7–10	5–12
CrN (CrAlN) coating	5.90	1770	~9.0	2–5
Ti ₂ AlC	4.00	>3000 (decomposition)	~8.5	46
Cr ₂ AlC	5.24	~1500 (decomposition)	~12.5	22
V ₂ AlC	4.87	–	~9.4	45

Note: RT represents room temperature.

vulnerability to grid-to-rod fretting failure.¹⁹ A wide variety of materials have been proposed and examined as protective coatings on Zr alloys. The principal coating concepts can be broadly divided into three categories: metallic coatings, ceramic coatings and multilayer coatings, as summarized in **Table 1**. Some less relevant coating concepts or surface modification methods are not considered here.¹⁰ Nearly all coating concepts consider only protection of waterside (outer) surfaces of the cladding tube. In case of accidental scenarios such as LOCA with ballooning and burst of the cladding, oxidation of fuel side (inner) surfaces may become significant as well. To our knowledge, only one group focused on enhanced protection of the inner surface based on amorphous Cr-based coatings deposited by DLI-MOCVD (direct liquid injection of metal organic precursors chemical vapor deposition) process.^{20,21}

Coating materials with low density, high melting point and thermal conductivity, comparable thermal expansion coefficient to Zr alloy substrate and low neutron absorption cross section are favorable.²² **Table 2** gives the values of some notable properties of these coating materials, together with Zircaloy-4 as comparison (mainly adopted from MatWeb database). Both single metallic element and intermetallic/alloy have been examined. A pure metallic chromium coating represents an attractive and encouraging choice as a near-term ATF solution for implementation considering its satisfactory compromise of performance under both normal and accident conditions. Thus, Cr coatings are being intensively pursued by both academia and industry.^{23–56} Among the metallic materials, one new alloy concept denoted as high entropy alloys (HEA) (or multi-principal component alloys) was explored recently.⁵⁷ HEAs are loosely defined as solid solution alloys that comprise at least five principal elements in equal or near equal atomic concentration.⁵⁸ The specific random arrangement of atoms in HEAs endows them some exceptional physical and mechanical properties.⁵⁸ Metallic coating materials typically offer the benefits of excellent adherence, high toughness and ductility, high thermal conductivity and easy fabrication. However, they normally possess low melting temperature or low eutectic reaction temperature with underlying Zr alloy substrate, challenging their performances during accident scenarios.

Ceramic coatings investigated include oxides, carbides, nitrides and one family of ternary-layered compound $M_{n+1}AX_n$ (MAX, n typical 1–3) phases. The MAX phase (M: early transition metal, A: mainly A-group element and X: C and/or N) materials are layered, hexagonal carbides and nitrides.^{59,60} Their crystal structures can be viewed as different transition metal carbide or nitride layers interleaved by pure A-element layer. They have attracted increasing attention in recent decades because of their unique combination of metallic and ceramic properties. Ceramics generally exhibit excellent corrosion resistance and radiation tolerance, high hardness and good wear resistance.^{10,61} One critical challenge to be evaluated for ceramic materials as protective coating is their brittle characteristics and low fracture toughness, making them susceptible to cracking/spallation when suffering high stresses.

To overcome or alleviate the limitations of a single-layer metallic or ceramic coating, many multilayer coating designs have been proposed, as shown in **Table 1**. For instance, a thin metallic layer as a bonding interlayer aims to improve the adhesive strength of ceramic coatings^{62,63}; diffusion barriers were designed to alleviate the eutectic reaction or rapid interdiffusion between the coating and the Zr alloy substrate during high-temperature oxidation.^{52,64} Since silica and alumina are unstable and undergo hydrothermal dissolution as silicic acid (H_4SiO_4) and aluminum oxy-hydroxide ($AlO(OH)$), respectively, during normal operation conditions

(see Section 4.17.4.1), functional layered coatings consisting of both corrosion- and oxidation-resistant layers simultaneously in a multilayer sequence were proposed.^{65,66} In addition, multilayer coatings often provide enhanced mechanical properties and corrosion performance compared to single layer coatings; the repetitive re-nucleation mechanism of defects at each interface enable interfaces to act as barriers to restrain the expansion and propagation of undesirable defects, such as micro-cracks and pores, within the coatings.^{67,68} However, the interfaces could diminish heat transfer in the coatings; for example, reduced thermal conductivity with increasing sublayers (interfaces) have been observed in TiN/TiAlN multilayer coatings.⁶⁹ Moreover, the multilayer designs add complexity in fabrication procedure and quality control of the coatings.

4.17.3 Deposition/Fabrication Methods

Several fabrication technologies have been used to deposit coatings on Zr alloys; the nature and performance of coatings depend significantly on the adopted fabrication technology and concurrent processing parameters. Physical vapor deposition (PVD, including magnetron sputtering, cathodic arc evaporation, electron beam evaporation, pulsed laser deposition, ion plating) and spraying (like cold spraying, plasma spraying and high velocity oxygen fuel (HVOF) spraying) represent the two most popular application methods for ATF claddings.¹⁰

In the PVD process, coating materials are vaporized from a solid or liquid source by heat or by bombardment with energetic particles in a vacuum or low-pressure gaseous (plasma) environment and finally condense onto the substrate.⁷⁰ Most PVD methods can coat the substrate at low temperatures (typically below 500°C) with dense, smooth and relatively thin layers (5–30 µm). The low deposition temperature and thin coating thickness are preferred with respect to the negligible impact on the microstructure of the cladding substrate and on the neutronic penalties inside the core, respectively.^{66,71,72}

In spraying processes, material particles or droplets are accelerated to high velocities and impinge on the surface of the substrate to form a coating via kinetic energy transfer. Depending on the processing temperature of the feedstock powder, cold spraying and thermal spraying processes exist. Most sprayed coatings for the ATF application adopted cold spraying because of its low process temperature and minimal oxidation. Spraying methods normally fabricate thick coatings (> 30 µm) with a high deposition rate, but with the drawbacks of less uniform and less dense layers. Fig. 1 displays typical microstructures of one metallic coating (Cr) and one ceramic coating (Ti₂AlC) on Zr alloys deposited by PVD and cold spraying. The noticeable differences in the microstructure of same type of coatings deposited via distinct methods can be seen. An uneven surface and coating/substrate interface (presence of Kelvin-Helmholtz perturbations)^{73,74} and some porosity exist for the cold spraying coatings. To fulfill the required

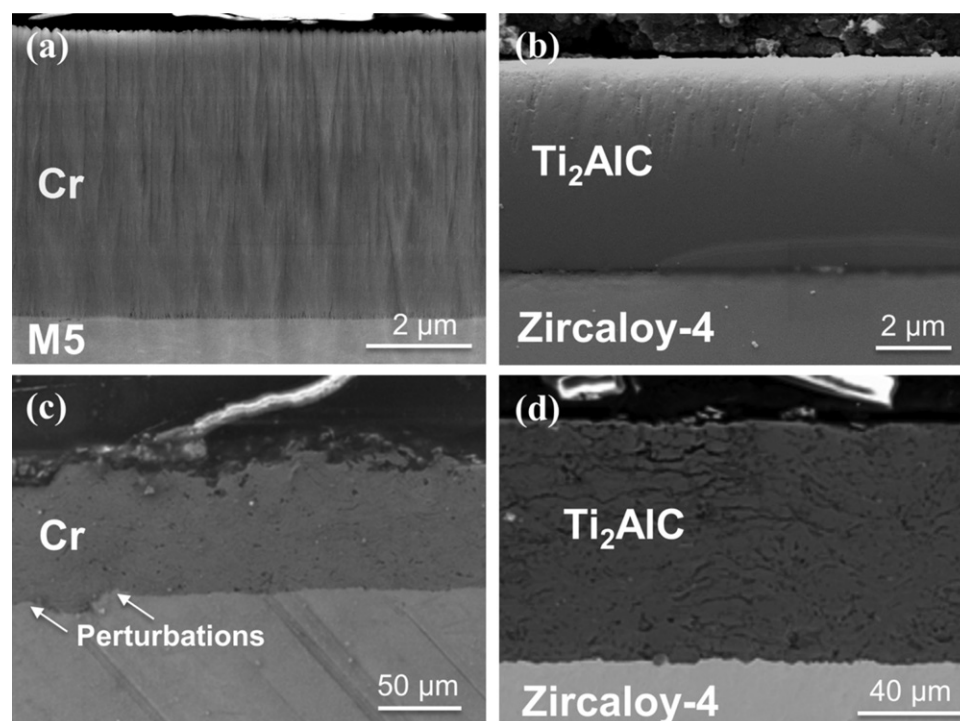


Fig. 1 Typical microstructures of metallic (Cr) and ceramic (Ti₂AlC) coatings on Zr alloys deposited by different processes: (a) and (b) PVD process; (c) and (d) cold spraying process. Reproduced from Brachet, J.-C., Idarraga-Trujillo, I., Flem, M. Le., *et al.*, 2019, *J. Nucl. Mater.* 517, 268–285. Wang, Y., Zhou, W., Wen, Q., *et al.*, 2018, *Surf. Coat. Technol.* 344, 141–148. Tang, C., Grosse, M.K., Trtik, P., *et al.*, 2018, *Acta Polytech.* 58, 69–76. Maier, B.R., Garcia-Diaz, B.L., Hauch, B., *et al.*, 2015, *J. Nucl. Mater.* 466, 712–717.

surface quality, a post-polishing process has been developed to smooth cold-sprayed Cr^{32,54} or FeCrAl⁶⁴ coatings. In addition, the mechanical impact of the high-velocity particles in the cold spraying process may result in a high level of residual stresses and severe plastic deformation of the bulk surface,⁷³ altering the mechanical characteristics of the substrate (see Section 4.17.4.2).

Chemical vapor deposition (CVD) and laser cladding technology have also been used for deposition of coatings on Zr alloys. The CVD process involves decomposition and/or reaction of volatile precursors to yield the desired films on the surface of substrates via chemical reaction at relatively high temperatures.¹⁵ For instance, Kaushal *et al.* attempted to deposit SiC coatings on Zr alloy substrate using a synthesized organosilicon precursor at 900°C.⁷⁵ Certain proprietary low temperature plasma-enhanced CVD (PE-CVD) techniques have been developed; for example, synthesis of a SiC coating at approximately 370°C⁷⁶ and polycrystalline diamond film at approximately 600°C.⁷⁷ Michau *et al.* successfully coated the inner surface of cladding tube with Cr-based coatings (Cr, CrC or CrSiC) by DLI-MOCVD at around 500°C.²¹ Typically, reducing the deposition temperature in CVD will simultaneously diminish the deposition rate.⁷⁸ Thus, the efficiency and homogeneity of the coatings deposited by these low-temperature CVD processes need further assessment. Laser cladding technology uses a powerful laser beam to melt the injected powder to form, after solidification, a coating layer. Cr, CrAl and Ni–Zr intermetallic/ceramic reinforced composite coatings have been fabricated on Zr alloys by this technology.^{26,79,80} This method offers the benefits of high deposition rate with highly dense and adherent coatings, but less uniformity. The effects on structural performances of the substrate due to heating effect have to be established.

Some other methods, including electroplating,⁸¹ plasma electrolytic oxidation⁸² and pre-oxidation,⁸³ are occasionally used. Additionally, surface modification using laser beam scanning to produce an oxide dispersion strengthened (ODS) structure on the Zr alloy surface before coating deposition for improving the high temperature strength was investigated.^{84,85} These methods, however, appear to be less attractive for practical applications due to some undesirable features (for instance coatings that are too thick or too rough, high processing temperatures, etc.).

To achieve optimized performance, the coating processes are normally subjected to an optimization procedure. For technical application, adjusting the process parameters to improve deposition efficiency and to optimize coating performances are regularly carried out.^{37,53,55,62,86} Deposition of phase-pure MAX phase coatings often remains a challenging issue due to their highly ordered crystal lattice structures and potential growth of many competitive compounds.⁶⁰ Recently, Tang *et al.* demonstrated that textured and single Cr₂AlC and Ti₂AlC MAX phase coatings can be synthesized on Zr-alloy substrates via controlled thermal annealing of magnetron-sputtered nanoscale elemental multilayers.⁸⁷ However, the successful transfer of this laboratory-scale process to industrial application level needs to be proved. The feasibility of fabricating full-length Cr-coated cladding tubes via PVD was recently demonstrated.⁴⁵

4.17.4 Performance Under Normal Operation Conditions

While enhancing the accident tolerance of fuel claddings is desired, one prerequisite is that the coatings should withstand the harsh environments inside the reactor core during normal operation.

4.17.4.1 Hydrothermal Corrosion Behavior

Pressurized water is used as the coolant in light water reactors. Depending on the type of the reactor, three distinct water chemistry environments exist, i.e., PWR (pressurized water reactor, ~330°C, 15.5 MPa), BWR (boiling water reactor, ~285°C, 7.5 MPa)-NWC (normal water chemistry) and BWR-HWC (hydrogen water chemistry). The water chemistry is optimized via minor additives to ensure reliable performance of reactor components.

The combination of high temperature and pressure results in coolant water in a subcritical state that acts as a highly corrosive medium. Thus, the waterside surfaces of the fuel claddings are exposed to hydrothermal corrosion. Many metallic or non-oxide ceramic materials are converted into their oxides or dissolve rapidly during hydrothermal corrosion in hot water.⁸⁸ Materials (exclusive of oxides) enable good hydrothermal corrosion resistances that can grow a passivation oxide layer acting as an effective diffusion barrier. The nature of a material, mostly metals, undergoing electrochemical corrosion in aqueous solutions can be predicted by Pourbaix diagrams, i.e., electrochemical potential versus pH diagrams for a given temperature, pressure and dissolved ion concentration via thermodynamic calculations.⁸⁹ Fig. 2 displays the Pourbaix diagrams of Si, Al, Ti and Cr at 350°C, 25 MPa and 10⁻⁶ mol/kg (typical operating conditions for PWR with slightly higher pressure), as examples. The diagrams can be classified into three regimes of immunity, passivity, and corrosion according to the identities of the dominant species: unreacted metal, stable surface oxide, and aqueous ions, respectively. Obviously, under typical PWR normal conditions as shown in Fig. 2, SiO₂ and Al₂O₃ are non-stable via formation of soluble aqueous ions. Rapid hydrothermal dissolution or selective leaching of these two elements (or oxides) may happen for Si- and Al-containing coatings. Metallic Ti and Cr (plus Zr, Fe and Ni^{10,89-91}) or compounds of corresponding metal-based coating materials are expected to form a stable, passive oxide layer. As summarized below, the corrosion performance of coating materials examined under simulated PWR normal conditions are largely consistent with the chemical nature predicted by Pourbaix diagrams.

4.17.4.1.1 Metallic coatings

Al and Si: To date, the hydrothermal corrosion behavior of pure Al and Si coatings on Zr alloys has not been reported. However, Park reported that amorphous alumina coatings were not stable and converted to γ -AlO(OH) (Boehmite) during autoclave

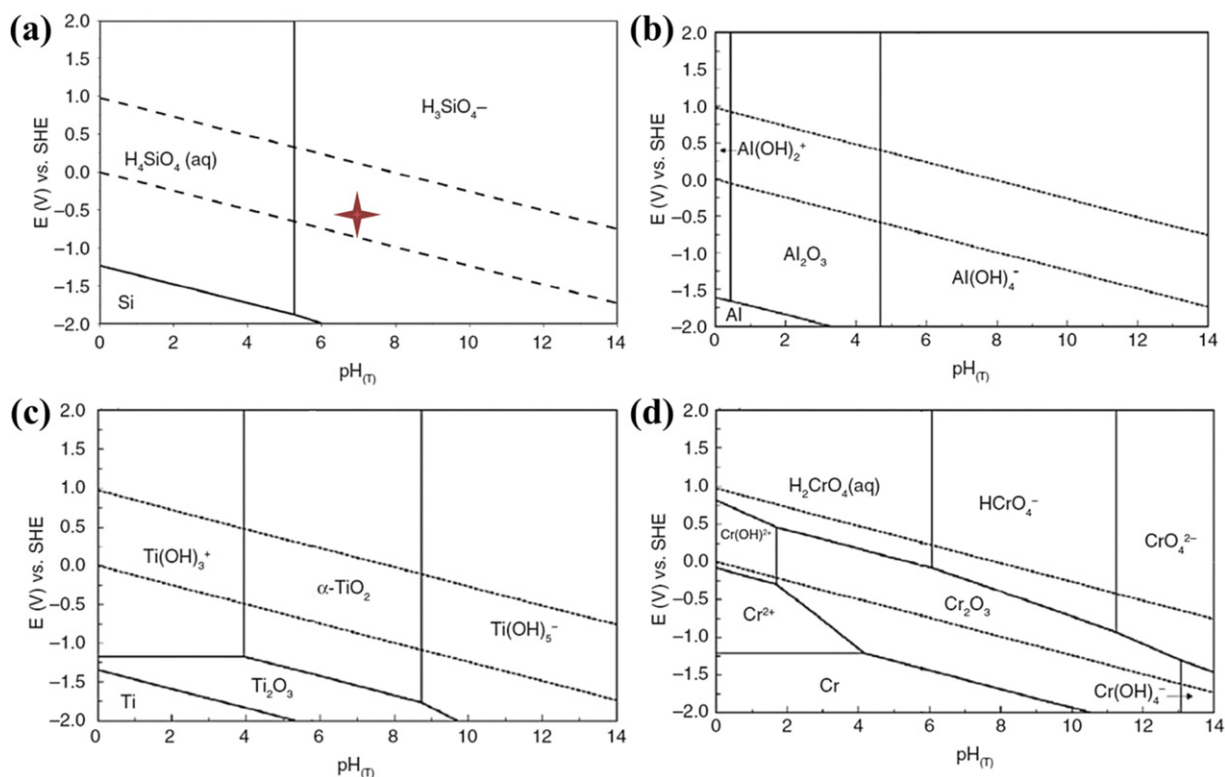


Fig. 2 Pourbaix diagrams for (A) Si, (B) Al, (C) Ti and (D) Cr at 350°C, 25 MPa and 10^{-6} mol/kg. SHE indicates standard hydrogen electrode. The electrochemical potential and pH for the aqueous solution in PWR core are approximately -0.5 V_{SHE} and 7.0, respectively, marked as star symbol in (A). Reproduced from Tang, C., Stueber, M., Seifert, H.J., Steinbrueck, M., 2017. Corros. Rev. 35, 141–166.

exposure at 20.1 MPa and 343°C.⁹² The hypothesized mechanisms were the dissolution of amorphous alumina and subsequent re-precipitation of boehmite during the cooling process. Kim *et al.* have tested bulk Si wafer and SiO₂ samples in a pressured water condition at 18.9 MPa and 360°C; rapid dissolution was confirmed for both samples.²⁶ Thus, pure Al and Si (as well Al₂O₃ and SiO₂) coatings, as expected, cannot survive under normal operating conditions.

Cr: Formation of a superficial, thermodynamically stable Cr₂O₃ layer bestows the Cr-coated claddings with an extremely low corrosion rate under simulated normal operational conditions, as experimentally proven by several groups.^{26,41,48,53} **Fig. 3** compares the mass gain and oxide scale thickness between uncoated and PVD Cr-coated Zr alloys during hydrothermal corrosion in an autoclave. A considerably lower mass gain of the Cr-coated claddings compared to the uncoated ones was confirmed under both PWR water chemistry and WWER (Russian PWR) water environments during long-term exposure. The thickness of the oxide scale formed on a Cr coating is roughly one order of magnitude thinner than the ZrO₂ layer growth on an uncoated alloy after exposure at 360°C and 18.7 MPa for 60 days, as shown in **Fig. 3(b)** and **(c)**. Similar results were obtained during autoclave tests of PVD Cr coatings at 415°C and 10 MPa, cold spraying and laser cladding Cr coatings under PWR conditions. The Cr₂O₃ layer can also act as a more efficient hydrogen diffusion barrier, lowering the hydrogen pickup of the cladding matrix during normal operation.⁴⁸ Therefore, Cr-coated claddings will be more tolerant to hydrogen embrittlement and allow for increased operational margins and higher fuel burnup.

During fuel rod insertion and fuel assembling, surface coatings may be scratched or scraped away locally. Coating technology thus should demonstrate that any defects, like cracking or spallation, in the coatings do not negatively affect the benefits of the coating or the performances of the underlying substrate (for instance the bimetallic effect via exposed interfaces accelerating the corrosion rate of the substrate⁹³). Brachet *et al.* investigated the impact of pre-existing defects (i.e., cracks in as-deposited coatings) on the corrosion performance of PVD Cr coatings on M5.²⁷ After autoclave testing under PWR conditions for 60 days, as shown in **Fig. 4**, the cracks had only a limited and localized impact without spallation of the coatings or accelerated corrosion of the underlying Zr alloy substrate. Nevertheless, longer exposures, at least up to one refueling cycle, are still required to verify the findings.

CrAl alloy: **Fig. 5** compares the weight gain and oxide scale thickness between uncoated and PVD CrAl (15 wt% Al) coated Zircaloy-4 tested in PWR conditions.⁸⁵ After exposure for 240 days, a homogeneous oxide layer of less than 1 μm consisting of 35 at% oxygen, 7 at% aluminum and 58 at% chromium grew on CrAl coatings. In comparison, a ~4 μm cracked oxide layer formed on the uncoated, inner side of the Zircaloy-4 tube. Formation of low-Al (Cr, Al)₂O₃ solid solution may inhibit dissolution of the Al during hydrothermal corrosion of the CrAl (15 wt% Al) alloy.⁹⁴

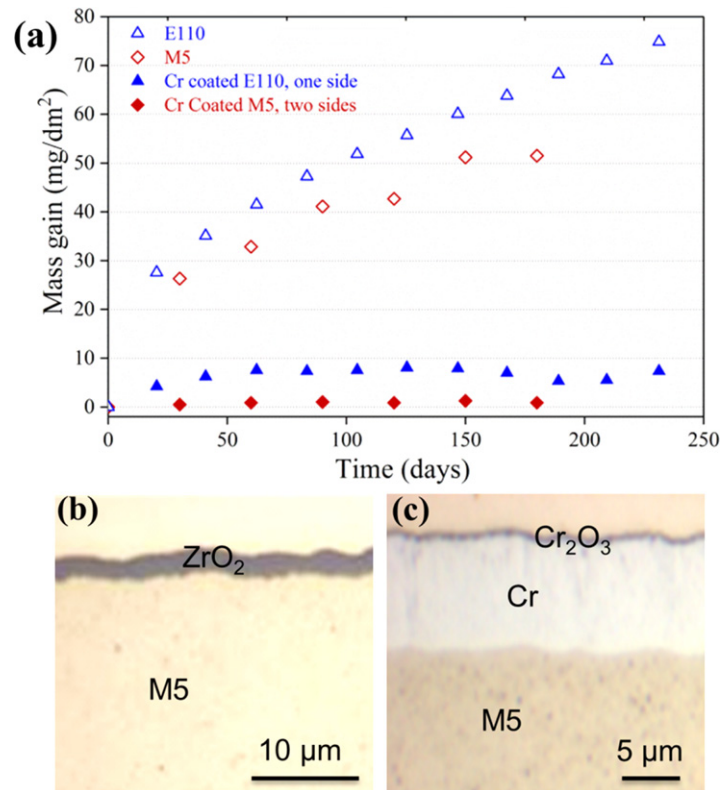


Fig. 3 Comparison of mass gain and oxide scale thickness between uncoated and PVD Cr-coated Zr alloys after hydrothermal corrosion in autoclave testing. (a) Mass gain rate, M5: PWR water chemistry at 360°C, 18.7 MPa and E110: WWER environment at 360°C, 19.7 MPa; cross-sectional metallographic observations of (b) uncoated and (c) Cr coated M5 after exposure for 60 days. Courtesy Brachet.

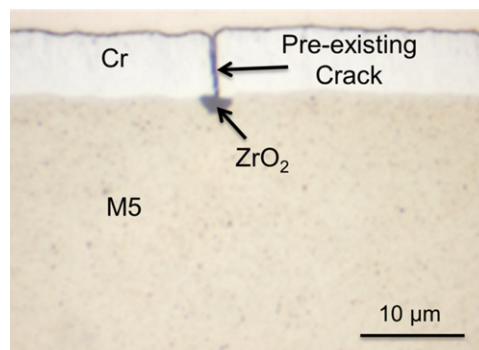


Fig. 4 Cross-sectional micrograph of PVD Cr-coated M5 with a pre-existing crack through the coating after autoclave testing for 60 days. Courtesy Brachet.

FeCrAl alloy: FeCrAl alloys have been proposed as protective coatings considering their exceptional oxidation resistance arising from selective oxidation of Al at elevated temperatures. Hydrothermal corrosion tests in autoclaves revealed that both FeCrAl bulk and coatings possess good corrosion resistance via growth of primarily spinel-type oxides consisting of Fe and Cr,^{95–97} as displayed in Fig. 6. In the case of coatings, a transition layer (Fe- or Cr- based oxide phases) grew inwardly between the spinel oxide layer and the FeCrAl layer. Long-term exposure of bulk FeCrAl alloys found dissolution of the Fe-rich spinel oxides in hydrogen water chemistry. Overall, the thickness loss rate, a maximum ~2 µm after one year in the absence of irradiation, is inconsequential with regard to the thick cladding. However, in case of thin coatings the dissolution rate and associated microstructure evolution during long-term exposure needs to be assessed.

Zirconium silicides: Zirconium silicides with different stoichiometries (Zr₂Si, ZrSi, and ZrSi₂) have been proposed as protective coatings on Zr alloys and the hydrothermal corrosion behavior of ZrSi₂ bulk and coating was reported.^{98–102} Fig. 7 shows images of bulk ZrSi₂ and ZrSi₂ coatings on Zr alloy substrate after autoclave exposures at 400°C and 10.3 MPa for 72 h. The corroded bulk ZrSi₂ surface revealed cracks and pores, attributed to selective leaching out of Si during exposure. Similar findings were confirmed

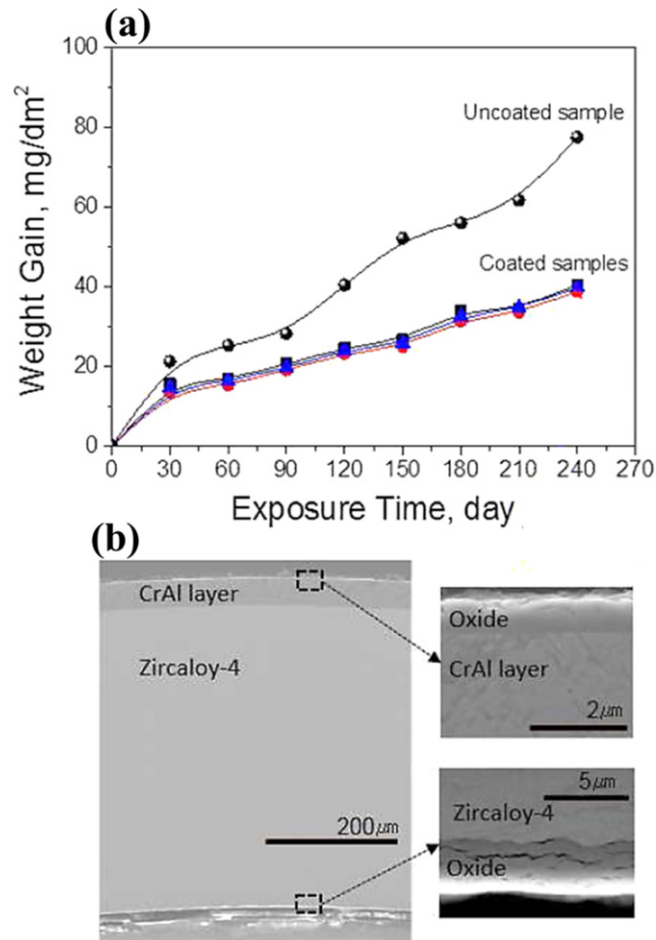


Fig. 5 Comparison of (a) weight gain and (b) oxide scale thickness (240 days) between uncoated and PVD CrAl (15 wt% Al) coated Zircaloy-4 in PWR simulation loop condition at 360°C and 18.9 MPa. Reproduced from Kim, H.G., Kim, I.H., Jung, Y.I., *et al.*, 2018. J. Nucl. Mater. 510, 93–99.

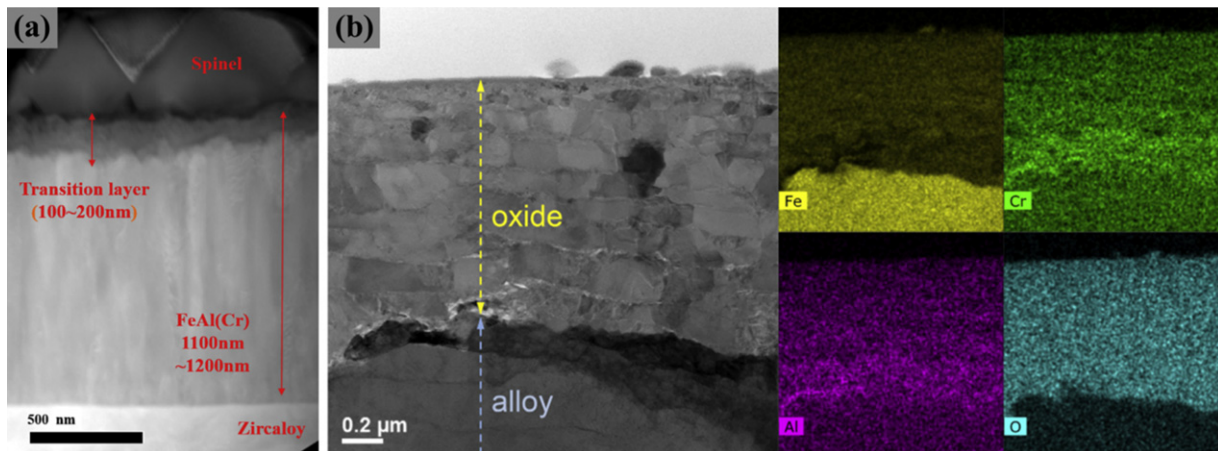


Fig. 6 Cross-sectional images of (a) Fe₄Cr₃₄Al (at%) coating on Zr alloy after exposure at 288°C and 9.5 MPa, BWR condition for 20 days, (b) bulk Fe₁₀Cr₅Al (wt%) alloy after one year of immersion at 330°C and 15 MPa, PWR condition with EDS mapping. Reproduced from Zhong, W., Mouche, P.A., Han, X., *et al.*, 2016. J. Nucl. Mater. 470, 327–338. Terrani, K.A., Pint, B.A., Kim, Y.J., *et al.*, 2016. J. Nucl. Mater. 479, 36–47.

for the ZrSi₂ coatings, which exhibited significant recession and developed a porous and delaminated ZrO₂ surface layer. The hydrothermal corrosion performance of ZrSi₂ is not adequate.

AlCrMoNbZr alloy: An AlCrMoNbZr high-entropy alloy with nearly equal molar ratios was investigated as a protective coating on Zr alloys.⁵⁷ The magnetron sputtered coating was composed of a composite of amorphous and bcc-structured nanocrystals.

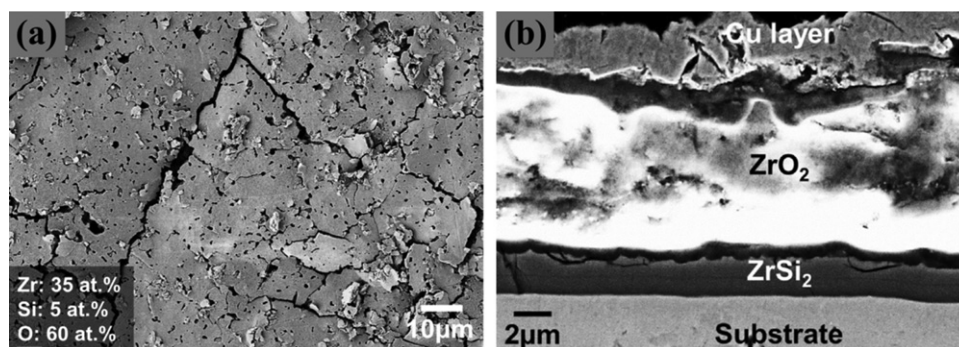


Fig. 7 Hydrothermal corrosion behaviors of ZrSi_2 bulk and coating. (a) Surface image of bulk ZrSi_2 and (b) cross-sectional image of ZrSi_2 coating on Zr alloy substrate after autoclave test at 400°C and 10.3 MPa for 72 h. Reproduced from Yeom, H., Lockhart, C., Mariani, R., *et al.*, 2018. *J. Nucl. Mater.* 499, 256–267.

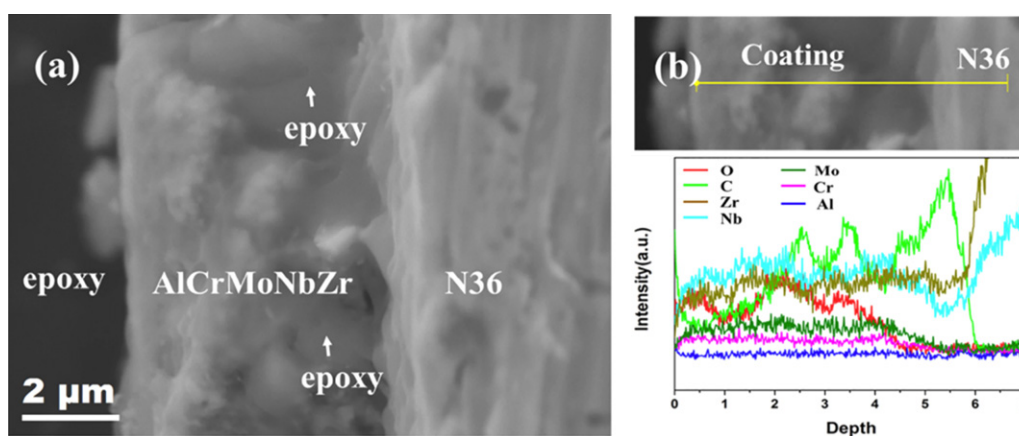


Fig. 8 Autoclave corrosion of the AlCrMoNbZr HEA coating on Zr alloy. (a) Cross-sectional image and (b) EDS line-scan after testing at 360°C and 18.7 MPa for 30 days. Reproduced from Zhang, W., Tang, R., Yang, Z.B., *et al.*, 2018. *Surf. Coat. Technol.* 347, 13–19.

After autoclave corrosion at 360°C and 18.7 MPa for 30 days, a protective oxide layer based on ZrO_2 and Cr_2O_3 was observed while significant loss of Al from the coatings was confirmed, as shown in **Fig. 8**.

4.17.4.1.2 Ceramic coatings

Oxides: As aforementioned, Al_2O_3 coatings^{17,92} are not stable and undergo rapid hydrothermal dissolution under normal operating conditions as demonstrated by several studies. Cr_2O_3 ¹⁰³ and ZrO_2 ⁸³ coatings, although not investigated, should be stable and exhibit good hydrothermal corrosion resistance based on existing Pourbaix diagrams (**Fig. 2**).

C: Nanocrystalline diamond (NCD) coatings deposited by CVD were proposed to enhance the corrosion and oxidation resistance of Zr alloys.^{77,78} After long-term exposure at 360°C and 16 MPa for up to 195 days, the coatings maintained their integrity and thicker NCD layers provided stronger protection of the substrate against hydrothermal corrosion and hydrogen uptake. The weight gain of the coated samples was decreased by 35%–55% and the hydrogen uptake of the coated samples also decreased significantly.

Carbides: SiC coatings proved to be unstable during autoclave tests simulating normal operations due to Si oxidation and rapid dissolution of SiO_2 ,⁷⁶ similar to other Si-containing coatings. Thus, Si-containing materials^{104,105} need proper design in ATF coating applications to avoid selective leaching of Si which can cause fast recession of the coatings during normal operations. The hydrothermal corrosion performances of other carbides (CrC and ZrAlC) coatings were not investigated and reported yet.^{21,106,107}

Nitrides: Transition metal nitrides are nowadays commercialized as hard protective coatings especially in the tooling industry. Two primary types of nitrides (TiN and CrN)^{19,62,63,108,109–112} are being investigated as protective coatings on Zr alloys. By incorporation of Al, coatings with better high-temperature oxidation resistance can be obtained.^{113–115} Superior hydrothermal corrosion resistance of binary TiN and CrN coatings was observed during corrosion testing in autoclaves.^{62,115} Furthermore, the coatings substantially reduced the hydrogen pickup by the Zr alloy substrate. However, the ternary TiAlN and CrAlN coatings demonstrated fast recession again due to rapid, selective dissolution of Al during exposure. One example is presented in **Fig. 9**, showing precipitation of $\text{AlO}(\text{OH})$ and significant depletion of Al in a TiAlN coating after just 3 days exposure. In comparison,

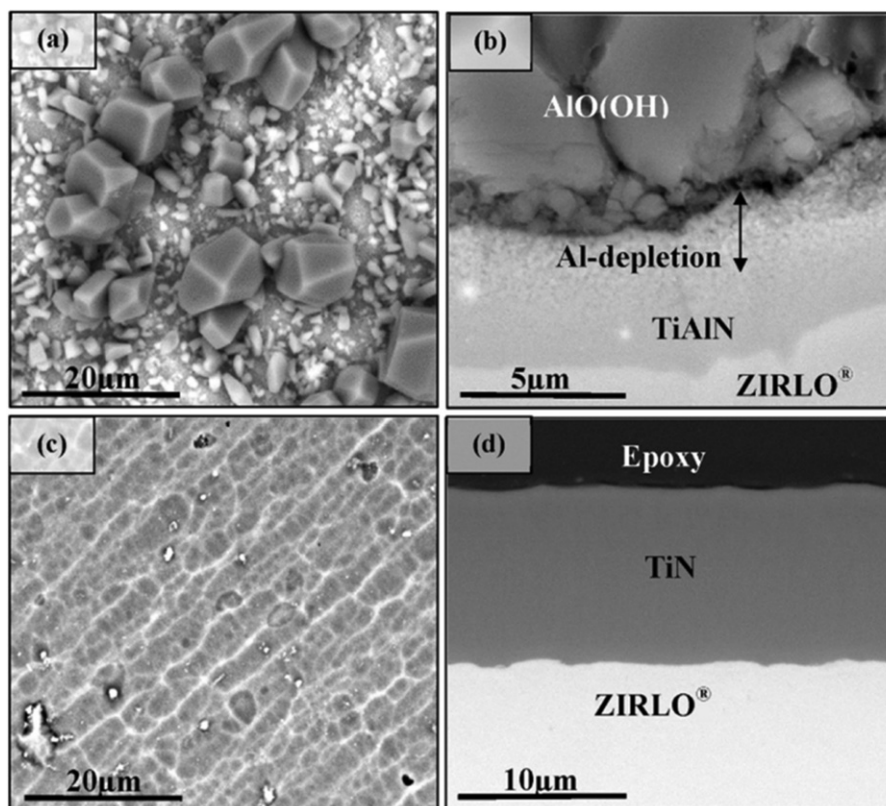


Fig. 9 Surface and cross-sectional images of coated ZIRLO samples after testing at 360°C and 18.7 MPa for 3 days; (a) and (b) TiAlN coating, (c) and (d) TiN coating. Reproduced from Alat, E., Motta, A.T., Comstock, R.J., *et al.*, 2016. J. Nucl. Mater. 478, 236–244.

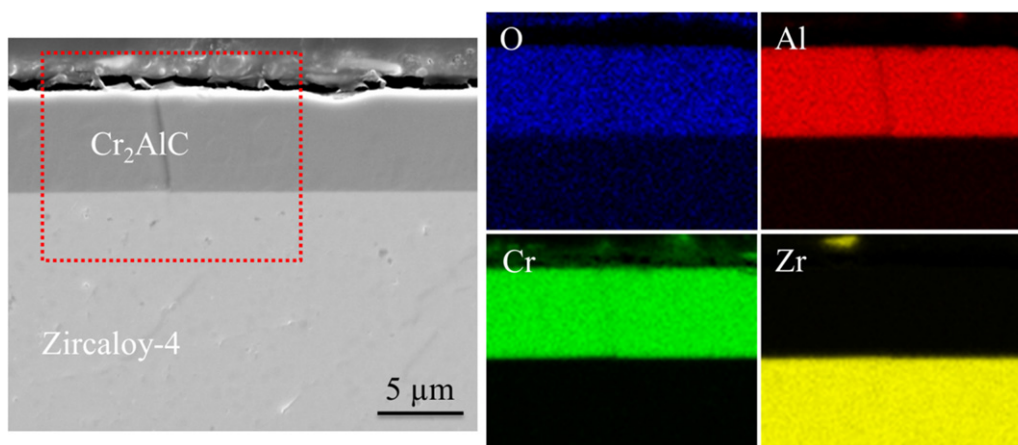


Fig. 10 Cross-sectional image and EDS mapping at the rectangular area of Cr_2AlC coated Zr alloys after autoclave testing at 360°C and 18.8 MPa for 3 days. An initial crack existed due to the high thermal expansion coefficient mismatch between the coating and the substrate.

uniform corrosion of TiN coating with a very thin oxide layer was observed. Multilayer coating concepts are being developed to resolve this issue.⁶⁵

MAX phases: Several alumina-forming MAX phases are interesting coating materials for the ATF application given their exceptional properties and excellent oxidation resistance as bulk materials.^{116–123} However, their hydrothermal corrosion performance is seldom investigated. **Fig. 10** shows Cr_2AlC coated Zr alloys after autoclave testing at 360°C and 18.8 MPa for 3 days. Parallel micro-cracks existed within the Cr_2AlC coating layer initially owing to the high thermal expansion coefficient mismatch between the coating and the substrate. The Cr_2AlC coating exhibited good corrosion resistance with no visible oxide layer and no depletion of Al, even at regions nearby the micro-cracks. Similar findings have been obtained during autoclave testing of bulk MAX phases Ti_3SiC_2 , Ti_3AlC_2 , Ti_2AlC and Cr_2AlC for a longer period, 28 days, at 300°C and 12 MPa. No obvious change of the Cr_2AlC

sample was found and the superior performance of Cr_2AlC could be attributed to the high Cr content allowing the formation of a passive chromia layer, thus inhibiting preferential removal of Al and further corrosion.¹²⁴ The other Ti-based MAX phases cannot form a passivating oxide layer in conjunction with preferential Al-layer (Al or Si) dissolution.¹²⁴ These findings suggest that Cr_2AlC represents an attractive option for ATF coating applications. Long-term autoclave tests are still required.

4.17.4.1.3 Multilayer coatings

Hydrothermal corrosion performances of some multilayer coating concepts have been investigated, especially those targeting to prevent the rapid dissolution of Al or Si during normal operations. Wiklund *et al.* have deposited Ti/TiN multilayer coatings on Zr alloys and the coatings demonstrated considerably enhanced corrosion and hydriding resistance during autoclave test at 360°C and 22 MPa for 200 days. A thick multilayer coating with numerous sublayers has proved favorable for optimal performance.¹⁸ As indicated earlier, many single-layer Al-containing coatings sustain quick failure via preferential dissolution of Al during hydrothermal corrosion. TiAlN/TiN,⁶⁵ CrAl/Cr¹²⁵ and AlCrMoNbZr/(AlCrMoNbZr)N^{126,127} multilayer structures have proven that the top layer can effectively stop Al migration and prevent boehmite phase formation during autoclave tests. Fig. 11 shows a cross-sectional view and corresponding EDS line scan of a TiAlN/TiN multilayer coating on a Zr alloy after autoclave testing as an example. The coatings, with a thin layer of TiN ($\sim 1\ \mu\text{m}$) as a barrier on the surface, showed minimal weight gain, superficial oxygen penetration and no boehmite phase formation.⁶⁵ The bi-layered $\text{ZrSi}_2/\text{Zr}_2\text{Si}$ coating concept was proposed to stabilize the Si during autoclave testing.⁹⁸ However, the coating was fully oxidized after exposure at 400°C and 10.3 MPa for 72 h.

4.17.4.2 Mechanical Properties

The mechanical properties of the coated claddings, especially their mechanical behavior during in-pile irradiation, are moreover particularly vital to enable their successful implementation.¹²⁸ Even though some separate-effect irradiation tests have been conducted and test/verification of lead test fuel rods (Cr coated) in research or commercial reactors are currently under way, no specific analyses of the mechanical behavior of coated claddings after irradiation have been reported yet. This section will summarize the available out-of-pile results concerning the mechanical properties of various coated cladding concepts without irradiation.

The surface mechanical properties of the coated claddings are expected to be improved considering the typical low thickness and specific microstructural features (like small grain size and unique stress state) of coatings. In other words, the coatings are normally harder than the Zr alloy substrates. The fretting and wear damage (grid-to-rod fretting and debris fretting) resistances thus can be enhanced compared to uncoated substrates during normal operations. For instance, PVD Cr^{44,45,51} and CrAl¹²⁹ coatings have demonstrated significantly improved wear resistance during grid-sliding test and debris wear test; one example is shown in Fig. 12. Similarly improved fretting-damage resistance was also reported for ceramic coatings, like TiN.¹⁹ However, brittle cracking and fracture were initiated before destroying the TiN coatings owing to its low toughness.

The bulk mechanical properties (like tensile, compression, elongation, creep, etc.) of the coated cladding should be comparable to the uncoated cladding if the coating thickness is sufficiently thin and the deposition/fabrication process does not change the Zr alloy microstructure. This is normally the case for thin coatings deposited by PVD at low temperature. However, for thick coatings deposited for instance by cold spraying, the microstructure and mechanical behavior of the substrate may possibly be modified.

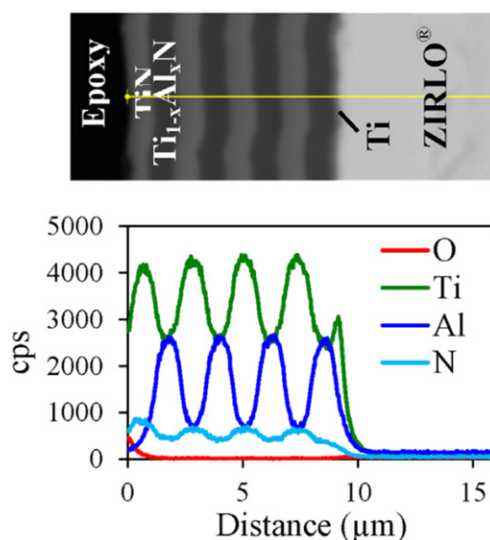


Fig. 11 Cross-sectional image and EDS line-scan of TiAlN/TiN coated Zr alloy after autoclave test at 360°C and 18.7 MPa for 33 days. Reproduced from Alat, E., Motta, A.T., Comstock, R.J., *et al.*, 2016. J. Nucl. Mater. 478, 236–244.

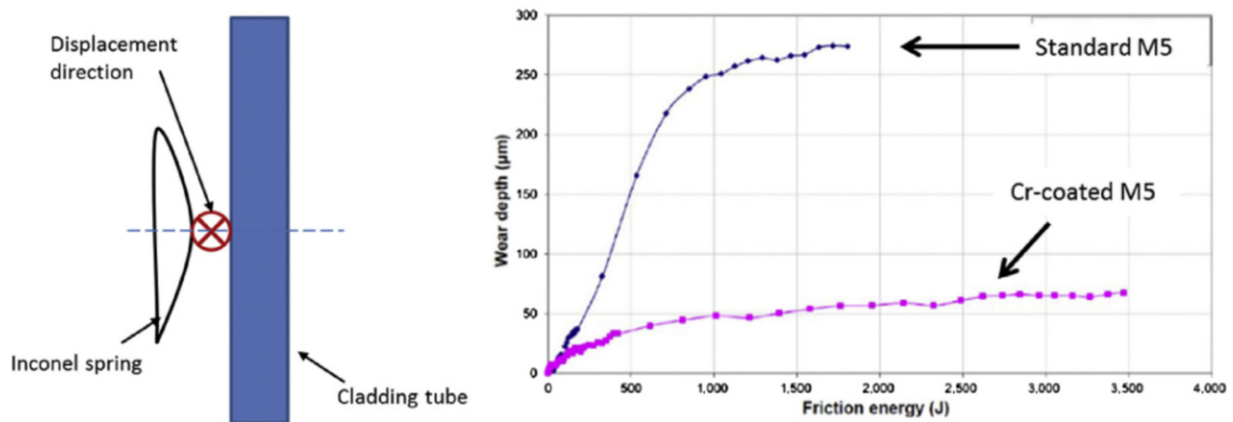


Fig. 12 Schematic representation of the experimental setup for the wear tests and comparison of total wear depth as a function of friction energy of uncoated and Cr coated M5. Reproduced from Bischoff, J., Delafoy, C., Vauglin, C., *et al.*, 2018. Nucl. Eng. Technol. 50, 223–228.

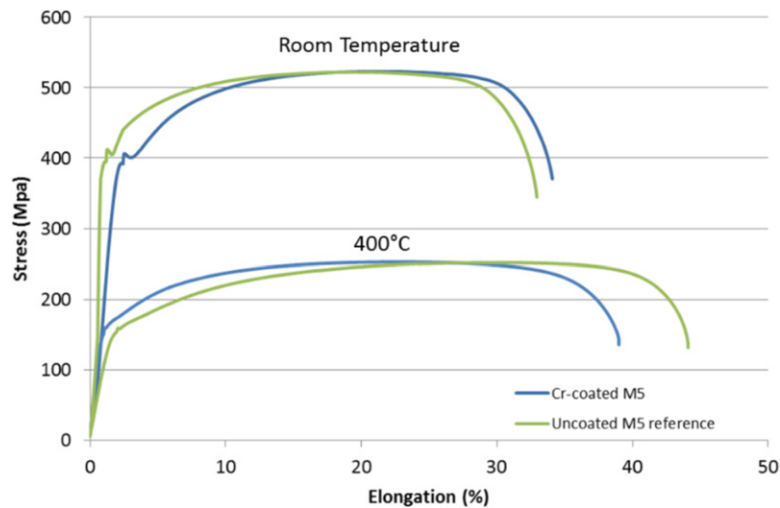


Fig. 13 Tensile tests at room temperature and 400°C of PVD Cr-coated M5 compared to uncoated reference M5. Reproduced from Brachet, J.-C., Idarraga-Trujillo, I., Flem, M.L., *et al.*, 2019. J. Nucl. Mater. 517, 268–285.

Fig. 13 shows an example of the stress-strain curves for PVD Cr-coated M5 and reference uncoated M5 tested at room temperature and 400°C.²⁹ The curves demonstrated similar mechanical behavior for both samples. Intensive investigations performed on Framatome's PVD Cr coating concept proved that the mechanical properties (yield strength 0.2%, ultimate tensile strength, and total elongation) of the Cr-coated samples all fell within the range of scatter from uncoated samples.^{29,45} Similar mechanical properties were also achieved between Cr coated claddings via laser²⁶ or cold spraying processes³² and uncoated reference samples. Peeling or spalling phenomena were not observed during ring compression and ring tensile tests of laser coatings and during tensile tests of cold spray coatings. The strength of the Cr-coated samples via laser processing was higher relative to the uncoated reference samples. Furthermore, as displayed in **Fig. 14**, the Cr layer demonstrated high adherence and good ductility, maintained a sound microstructure at up to 4% strain, whereas lateral cracks were formed after reaching 6% strain during ring tensile tests.²⁶ The total elongation at room temperature of the Cr-coated samples (18.5%) via cold spraying was lower than that of uncoated reference tubes (23.0%), but comfortably maintained the current minimum specified for cladding material (15%).³²

Some detrimental effects of coated claddings on mechanical behavior were occasionally observed especially for coatings deposited by the cold spraying process. The cold spraying process involves strong impact of the substrate via high velocity sprayed particles and significant plastic deformation of deposited coating particles.⁷³ Ševeček *et al.* investigated the fatigue behavior of cold sprayed Cr coated cladding and found that environmentally-induced cracks might initiate earlier for coated samples compared to uncoated reference samples in BWR-NWC condition. The premature crack initiation likely connects with the high-level of residual stress and stress concentration in the coating attributable to the inhomogeneities created by the cold spraying process.⁴⁷ Investigation of mechanical behavior of a Zr alloy coated with a FeCrAl/Mo (Mo as a diffusion barrier) layer deposited by cold spraying revealed enhanced hardness and cleavage fracture morphology of the Zr matrix directly below the Mo/Zr interface, which indicated the occurrence of localized deformation owing to Mo particle impact.⁷⁴

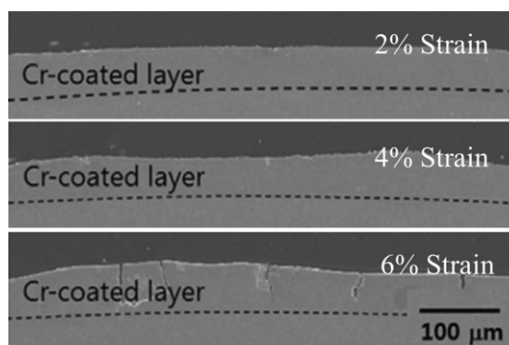


Fig. 14 Cross-sectional observations of Cr-coated Zircaloy-4 cladding tubes after ring tensile tests at 2%, 4%, and 6% strain. Coatings were deposited by a laser process. Reproduced from Kim, H.-G., Kim, I.-H., Jung, Y.-I., *et al.*, 2015. *J. Nucl. Mater.* 465, 531–539.

There is scarce information concerning the mechanical behavior of ceramic-based coatings on Zr alloy substrates. Nieuwenhove *et al.* reported that micro-cracks appear in a CrN coating at a strain level of about 1.5%.¹¹ Micro-tensile testing of TiAlN-coated Zr alloys found that transverse cracks within the coating layer start to appear at a strain level of 0.84%.¹¹³ Clearly, these values are much lower than that mentioned before for pure metallic Cr coatings ($\sim 6\%$). Ceramic coatings typically exhibit brittle characteristics and low toughness and thus are more prone to undergo damages like cracking and fracture.

4.17.4.3 Irradiation Performance

The structural integrity of the coating-substrate system will be highly challenged in the reactor core especially towards high fuel burnup considering well-known irradiation-induced degradation phenomena.^{128,130} Depending on the operational temperatures and damage levels, mainly five irradiation-induced degradation mechanisms exist for materials (i.e., irradiation hardening and embrittlement, phase instabilities, irradiation creep, volumetric swelling and He embrittlement).¹³¹ The coating and substrate regularly behave differently under irradiation owing to mismatches of their fundamental physical properties, such as strain mismatches in irradiation-induced growth and creep.¹²⁸ Additionally, the interfaces between dissimilar crystal structures with different lattice parameters are energetically favorable sinks for growth and aggregation of defect clusters. The hydrothermal corrosion or dissolution rate can be enhanced under irradiation conditions. Thus, the hydrothermal corrosion behavior of the coating-substrate system as well as the chemical and mechanical compatibility between the coating and the substrate under irradiation (in-pile) conditions needs thorough assessment and validation.

4.17.4.3.1 Out-of-pile behavior

Preliminary ion irradiation experiments were performed on some relatively mature coating concepts (mainly Cr-based) to simulate neutron-induced damage.

The interface structure and interface stability of a PVD Cr coated Zr alloy under irradiation were examined with damage at the interface of 10 dpa (displacements-per-atom) using 20 MeV Kr^{8+} ions.^{33,34} The results indicated primary coherent or semi-coherent crystallographic relationships of the Cr-Zr interface ensuring the adhesive strength of the coating. After irradiation, good chemical and microstructural stability of the Zr/Cr interface was confirmed without degradation of the interface and irradiation-induced diffusion of Cr into the substrate. The adhesion of the Cr coating to Zr substrate did not decrease after this specific ion irradiation. Irradiation of vacuum arc Cr coatings by 1.4 MeV argon ions to 25 dpa indicated radiation-induced isotropic growth of grains with formation of vacancy voids and radiation-induced swelling within the coatings.³⁸ Nevertheless, the swelling was observed at a low level (0.66%), demonstrating a high irradiation resistance of the chromium coatings. Maier *et al.* have examined the irradiation tolerance of cold sprayed Cr coatings via in-situ TEM using 1 MeV Kr^{+2} ions to 3 dpa.³⁵ Radiation-induced defects, such as black spots and dislocation loops, were observed. They suggested that the severely plastically deformed microstructure of the cold sprayed Cr delayed the onset and growth of radiation-induced defects.

Kratochvílová *et al.* have investigated the irradiation tolerance of a CVD polycrystalline diamond coating on Zr alloy substrate using 3 MeV Fe^{2+} to 10 dpa.¹³² After ion beam irradiation, the film did not reveal any microstructural changes and showed satisfactory structural integrity.

Energetic particle irradiation of TiN coatings using 134 keV Xe^{+} ions at 473K to 6.2 dpa revealed significant microstructural alterations with radiation-induced segregation of the coatings (TiN is prone to dissociate creating Ti-enriched zones).¹¹⁰ The nucleation and growth of Xe bubbles were believed to play a key role in its dissociation behavior. It is suggested that nanocrystalline TiN thin films may not be a suitable solution as protective coatings on Zr-based alloys.

Bugnet *et al.* investigated the ion irradiation of Cr_2AlC and Cr_2GeC coatings deposited on sapphire substrates with 320 keV Xe^{2+} focusing on single grains.¹³³ The results indicated that both compounds were amorphized at moderate fluence rates. Annealed cold spraying Ti_2AlC coating on Zr alloy substrate up to 923K resulted in formation of three interfacial intermetallic compounds (ZrAl_2 , ZrAl , and Zr_3Al). Ion irradiation to a damage level of 100 peak dpa disrupted the layered structure of the

Ti₂AlC coating while amorphization was observed for some of the intermetallic compounds together with hardening effect.¹³⁴ V₂AlC coatings deposited by magnetron sputtering on Zr substrate were irradiated using 500 keV He ions.¹¹⁹ The results showed that the He bubbles preferentially nucleated along the substrate-coating interface and resulted in reduced adhesion strength of the V₂AlC coating. Thus, optimizing the interfacial structure is of substantial importance for improving the irradiation resistance of the coating-cladding system.

The interface stability and mechanical properties of AlCrMoNbZr/(AlCrMoNbZr)N multilayer coatings with individual layer thickness of 5 nm, 10 nm and 50 nm, subjected to helium ion irradiations were studied.¹²⁷ He ion irradiation induced intermixing and chemical reactivity was observed in case of coating with lower modulation periods. Nanoindentation tests revealed decreased hardness of all multilayer coatings mainly due to the thermal effect caused by irradiation.

The irradiation resistance of other coating concepts is largely unexplored yet. The irradiation performance of some intensively investigated coating materials, like FeCrAl alloys and MAX phases, have been examined in bulk form, which can provide some glimpse of their behavior when applied as protective coatings. FeCrAl alloys with a high Cr addition are vulnerable to irradiation hardening and embrittlement, plus phase instabilities owing to the formation of Cr-rich α' precipitates.^{135,136} MAX phase materials generally exhibit strong tolerance to energetic ion and neutron irradiation damage.¹³⁷ However, different behaviors were seen experimentally. Irradiation-induced damages, like phase transition and amorphization, cracking and surface exfoliation, were sometimes observed.^{138–141} Thus, the behavior of FeCrAl and MAX phase coated Zr alloy systems under irradiation needs to be adequately addressed in the future.

4.17.4.3.2 In-pile behavior

A five-year irradiation program was launched in 2016 to test the in-pile behavior of PVD Cr-coated (Framatome) zirconium alloys (plus SiC_f/SiC composites) in the Gösgen nuclear power plant (PWR) in Switzerland.⁴⁶ Visual inspection after one cycle (one-year irradiation and corrosion) proved that the Cr coatings were very stable without indications of delamination. The Cr-layer showed essentially the same degree of homogeneity as before irradiation and a golden color corresponding to growth of a very thin Cr-oxide layer. Lead test rods (LTRs) of cold sprayed Cr coated claddings in commercial reactors led by Westinghouse are planned in spring 2019.¹⁴²

Irradiation campaigns of CrN, TiAlN and CrAlN coatings on Zr alloys have been conducted in the Halden Reactor (Norway).¹⁴³ Only the CrN coating survived and remained to a large extent (>80%) intact after exposure; both the TiAlN and CrAlN coatings disappeared from the fuel rod surface related to the rapid selective dissolution of Al. Some degree of damage corresponded to cracking and localized delamination of the CrN coating occurred, likely because of mechanical problems which led to overheating of the fuel-rod cladding. Zirconium oxide grew beneath the areas where the coatings were damaged, as shown in Fig. 15, confirming the loss of protectiveness in these areas.

4.17.4.4 Other Property Requirements

Coating solutions need to demonstrate compatibility with welding using current processes for bare Zr alloy fuel cladding. The welding performance of PVD Cr and CrAl coated claddings has been examined.^{48,51,85} Welded specimens also have been subjected to hydrothermal corrosion. Using the current resistance welding process, Bischoff *et al.* have shown welding of the Cr coated tube

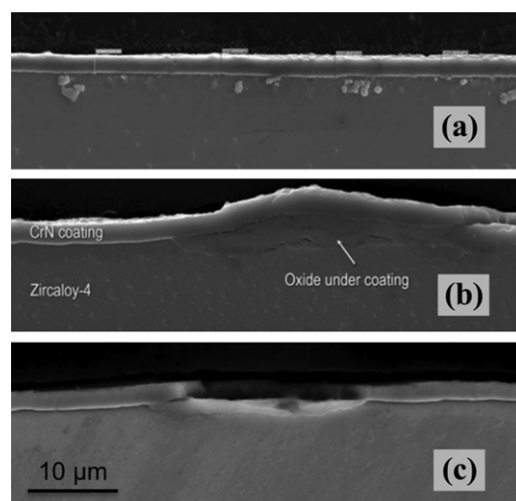


Fig. 15 Cross-sectional images of CrN-coated Zr alloy tube before (a) and after (b, c) irradiation in the Halden Reactor for 287 days. Zirconium oxide formed under cracked and delaminated coating areas. Reproduced from Van Nieuwenhove, R., Andersson, V., Balak, J., Oberländer, B., 2018. In-pile testing of CrN, TiAlN and AlCrN coatings on zircaloy cladding in the Halden reactor. In: Proceedings of the 18th International Symposium on Zirconium in the Nuclear Industry, pp. 965–982. West Conshohocken, USA.

without modifying the welding process.⁵¹ Localized spallation of the Cr coatings near the welding zone was reported by Krejci *et al.* after autoclave exposure for 210 days in WWER conditions using tungsten inert gas (TIG) welding.⁴⁸ The CrAl-coated cladding bonded well to the end cap without peeling or damage of the coating layer after friction welding and corrosion for 120 days in a PWR simulation loop.⁸⁵

The impact of a coating on surface wettability and heat transfer of the cladding tube has been infrequently investigated. Pure Cr coatings demonstrate a slightly higher contact angle with static water droplets compared to fresh Zr alloy surfaces.^{103,144} A much higher contact angle was seen for AlCrMoNbZr-based coatings⁵⁷ and a lower contact angle was measured for ZrSi₂ coatings.¹⁰¹ Enhanced wettability was observed after oxidation or after gamma irradiation of Cr coatings and for Cr₂O₃ coatings.^{28,145} Increased wettability and porosity of the coating layer could improve the heat transfer characteristics of the fuel cladding.^{103,144}

4.17.5 Performance Under Accident Scenarios

The anticipated key performance features of innovative ATF claddings for improved safety margins and increased coping time during accident scenarios are reduced oxidation kinetics in high-temperature steam/air with simultaneously minimized hydrogen generation and enthalpy input, together with improved strength to maintain core coolability and retain fission products.⁴ High-temperature oxidation resistance of materials relies on the growth of a thermodynamically stable oxide layer acting as a physical diffusion barrier between the reactant phases. The oxidation kinetics are determined by the chemical nature of the transport processes within the oxide scale. Fig. 16 shows the parabolic oxidation rates for various scale-forming bulk materials in steam as a function of temperature.⁷ It can clearly be seen that robust oxide scales for protecting the underlying matrix from fast consumption at elevated temperatures are those made of chromia, alumina or silica. Their growth rates decrease following the aforementioned sequential order. Even though chromia and silica can form volatile suboxides (in oxygen) or hydroxides (in steam) at elevated temperatures, their volatilization rates are normally sluggish in low-speed flow environments.¹⁴⁶ The other oxide scales, such as FeO_x, ZrO₂, NiO or TiO₂, are featured by much higher growth rates at elevated temperatures.¹⁴⁷

The oxidation mechanisms and degradation phenomena of oxidation-resistant coatings are essentially similar to bulk materials. Coating concepts not containing Cr, Al, or Si should not be suitable for ATF applications. However, additional constraints appear with coatings, mainly chemical and mechanical compatibility with the substrate, which may remarkably restrict their performance. Since coatings are normally thin, they contain a limited reservoir of the scale-forming element. Thus, interdiffusion/reaction between the coating and the substrate can deplete the scale-forming elements and introduce undesirable elements into both the coating and the substrate, deteriorating their oxidation resistance. Mechanical constraints, largely arising from thermal expansion mismatch, can also lead to premature degradation of the coating, such as by cracking and delamination. The mechanical properties (like ballooning, burst and fracture resistance, post-quench residual strength and ductility) of coated claddings are normally improved assuming reduced oxidation kinetics at LOCA relevant temperatures (below coating-substrate eutectic temperature). The performances of various coated cladding concepts during severe accidents have rarely been studied yet and, as-expected, are exceedingly challenging.

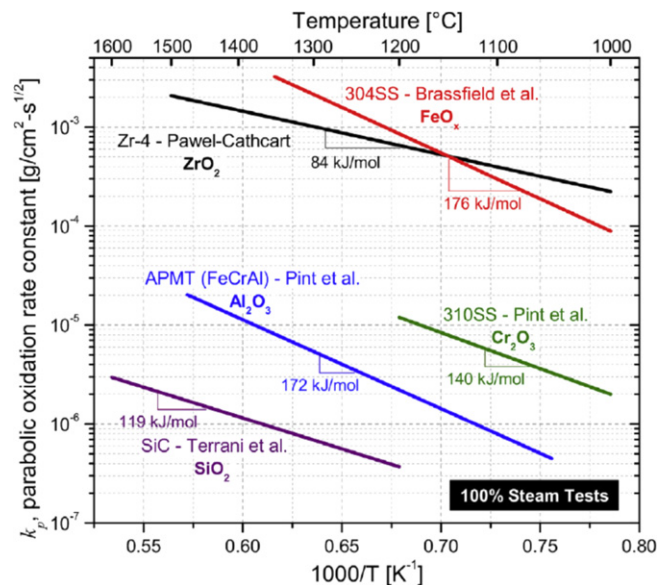


Fig. 16 Parabolic oxidation rates for various scale-forming materials in steam as a function of temperature. Reproduced from Terrani, K.A., 2018. J. Nucl. Mater. 501, 13–30.

4.17.5.1 Design-Basis Accidents

4.17.5.1.1 Metallic coatings

Oxidation of aluminum-modified Zr alloy surfaces (synthesized by magnetron sputtering of aluminum and subsequent thermal annealing) at 800°C in steam for 120 min displayed better oxidation resistance with average oxide layer thicknesses of $\sim 0.7 \mu\text{m}$ (around $8 \mu\text{m}$ for un-modified specimens). However, the oxide layer was slightly thicker for treated specimens after oxidation at 1000°C.¹⁴⁸ The poor oxidation performance of the coated surfaces is likely attributed to the formation of brittle intermetallics (see calculated phase diagram of Zr-Al in Fig. 17; Zr-Cr, Zr-Fe and Mo-Zr systems are also given¹⁴⁹) and surface cracks, preventing the growth of a continuous and uniform alumina scale.

The oxidation performance of thick Si coatings (up to 150 μm) fabricated by plasma spray with subsequent laser beam scanning treatment was investigated at 1200°C in steam.¹⁵⁰ The coated samples displayed improved oxidation resistance with $\sim 60\%$ mass gain compared to uncoated ones after exposure for 2000 s. However, here the coatings were too thick and as aforementioned, pure Si is unstable during normal operation.

Steam oxidation performance of Cr coatings, deposited by diverse methods, have been intensively examined.^{23,31,33,35,36,41,42-44,46,47,51-53} Generally, the high-temperature oxidation kinetics of Cr-coated Zr alloys is significantly reduced compared to uncoated alloys up to 1200°C relevant for LOCA scenarios. The coatings form a protective Cr_2O_3 scale during oxidation, demonstrating acceptable performance even under beyond design-basis conditions below the Zr-Cr eutectic temperature (1332°C, as shown in Fig. 17(b)). Fig. 18 compares the oxidation performance and mechanical behavior of PVD Cr coated and uncoated Zr alloys. Clearly, the oxide scale thickness on the Cr coating layer is one order of magnitude lower than that on bare Zr alloys during oxidation at 1200°C in steam, Fig. 18(c). Consumption of the coatings is determined by two combined processes, i.e., surface oxidation and inward diffusion into the substrate, as displayed in Fig. 18(d). The 12–15 μm Cr coating deposited by PVD can delay the oxidation of the Zr alloy substrate for approximately 5 h at 1100°C or 1 h at 1200°C in steam.⁴⁵ It is necessary to point out that at high water vapor partial pressure ($> 10 \text{ kPa}$) formation of volatile chromium oxyhydroxides becomes prominent, which further limits its protective capability to lower temperature ($\sim 1040^\circ\text{C}$).¹⁴⁶ The Cr-coated samples also demonstrated negligible reduction of residual strength and ductility before the complete consumption of the metallic Cr layer, Fig. 18(e), and improved ballooning and rupture

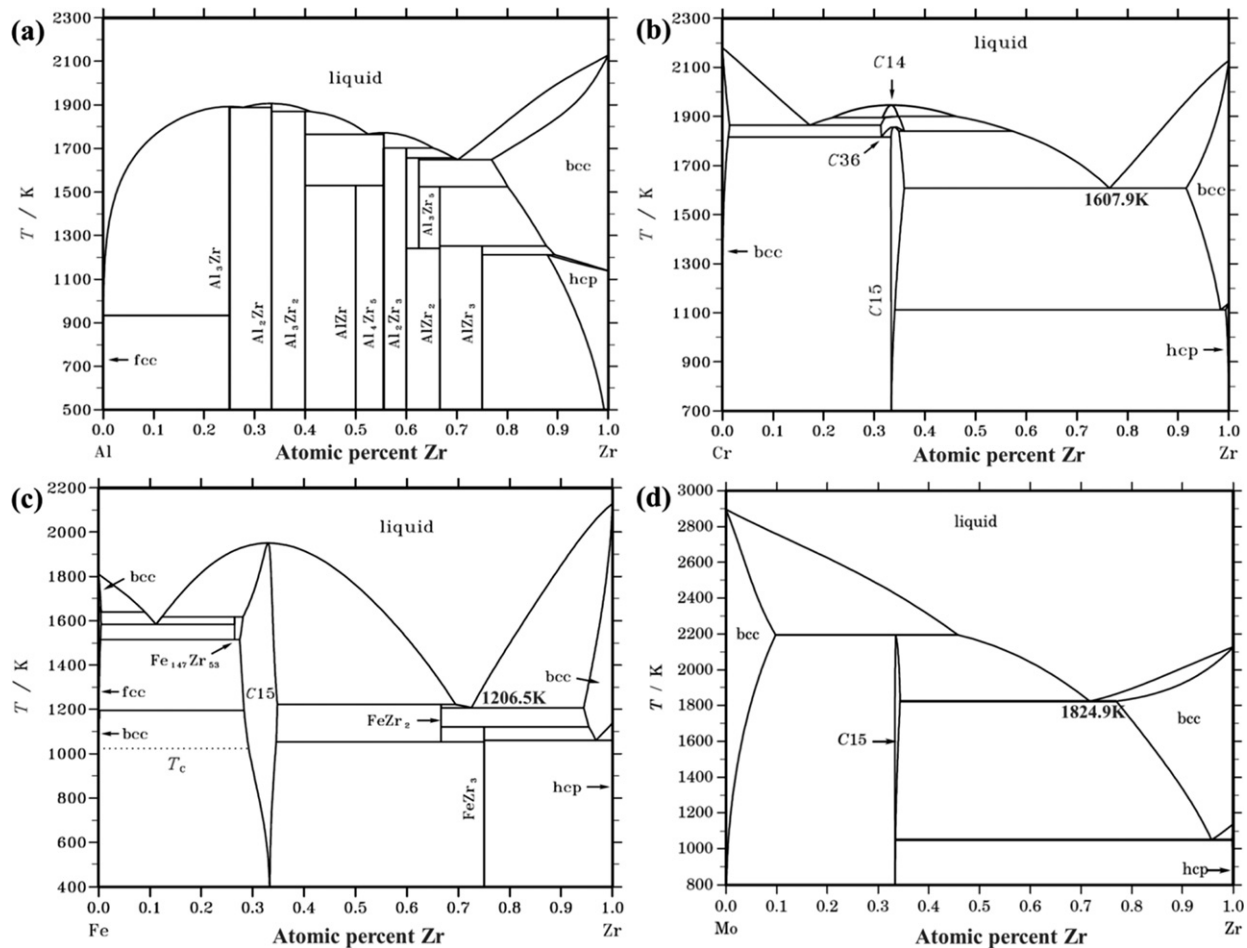


Fig. 17 Calculated phase diagrams of (a) Zr-Al, (b) Zr-Cr, (c) Zr-Fe and (d) Mo-Zr.

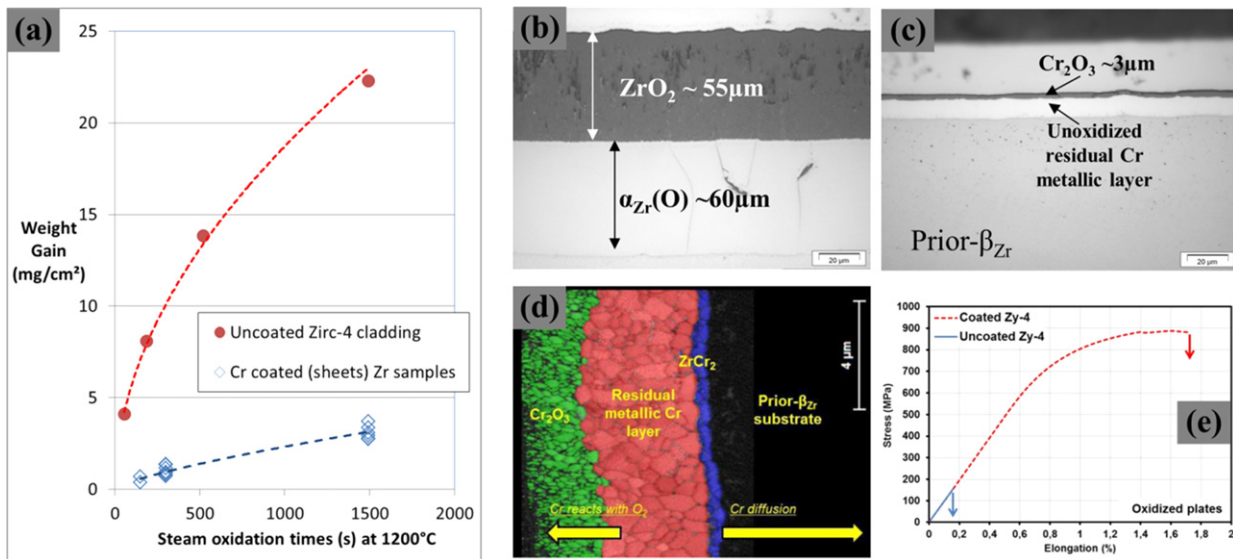


Fig. 18 Comparison of oxidation performance and mechanical behavior between PVD Cr coated and uncoated Zr alloys. (a) Oxidation rate, oxide scales on (b) uncoated Zircaloy-4 versus (c) and (d) Cr-coated samples after oxidation at 1200°C for 300 s in steam, (e) tensile stress-strain curves obtained at RT after two-side steam oxidation for 15,000 s at 1000°C. Reproduced from Brachet, J.-C., Idarraga-Trujillo, I., Flem, M. Le, *et al.*, 2019. *J. Nucl. Mater.* 517, 268–285.

resistance.^{26,50,55} In addition, the chromium coatings revealed high adherence without peeling including at the vicinity of the burst opening. The amount of hydrogen picked up by the cladding was significantly reduced simultaneously due to the existence of the Cr₂O₃ barrier. Similarly, enhanced oxidation and mechanical performances were reported for Cr coatings fabricated by other methods. However, during long-term scenarios inward diffusion of Cr could cause hardening and enhanced embrittlement of the cladding due to formation of brittle intermetallics.⁴¹ Han *et al.* found that the completely oxidized Cr coating can be reduced by the Zr substrate, revealing more complicated oxidation mechanisms.⁵⁶ In case of cold sprayed coatings, accelerated growth of initially existing cracks and bending of the coated tubes were observed during oxidation.⁴¹ Occurrence of these undesirable features needs to be addressed and avoided via coating optimization in the future.

Al- and/or Si-containing Cr alloys such as CrAl and CrAlSi were also considered as protective coatings, aiming to improve the oxidation resistance relative to pure Cr coatings. A CrAl (30 wt% Al) coating layer deposited via a laser coating process resulted in significant mixing of CrAl coating metal with the Zr substrate. The coatings demonstrated poor oxidation resistance because of considerable interdiffusion and formation of intermetallic compounds.⁷⁹ CrAl coatings deposited by PVD displayed much better oxidation performance. A metastable alumina layer developed on the CrAl coatings with Al composition over 43 at% during oxidation at 700°C in steam.³⁹ A 1 μm oxide layer (mainly Cr₂O₃) formed on CrAl (15 wt%)-coated cladding after oxidation at 1200°C for 3000 s in steam and water quenched.⁸⁵ Improved rupture resistance and post-quench ductility were also seen for coated samples.⁸⁵ Decreased oxidation rates of PVD CrAlSi coated specimens compared to bare Zr alloys up to 1200°C were reported.¹⁵¹ However, coating constituent elements (primary Al or Si) diffused substantially into the substrate and formed intermetallic phases with the Zr alloy substrate during oxidation.

Alumina-forming FeCrAl alloys (adequate addition of Cr and Al) are well known for their excellent high-temperature oxidation resistance and thus have been intensively investigated as protective coatings on Zr alloys. Formation of a protective alumina layer was confirmed during oxidation at relatively low temperature, such as 700°C in steam.⁹⁶ However, rapid degradation of the coatings without protection was seen once the oxidation temperature exceeds the Fe-Zr eutectic reaction temperature (around 930°C, Fig. 17(c)).¹⁵² Formation of interfacial intermetallic compounds at lower temperatures also embrittles the coated cladding.¹⁵³ Many efforts now attempt to identify a suitable interlayer as diffusion barrier.^{64,74,82,95,154}

Oxidation of zirconium silicide (Zr₂Si, ZrSi, and ZrSi₂) coatings revealed that ZrSi₂ possesses the best anti-oxidation behavior via formation of an oxide layer consisting of nanocrystalline SiO₂ and ZrSiO₄ in an amorphous Zr-Si-O matrix at 700°C in air.¹⁰⁰ However, the coatings have very limited improvement at higher temperatures. The incorporation of ZrO₂ into the scale during oxidation likely compromises the protective nature of the coatings.

4.17.5.1.2 Ceramic coatings

Durability of oxide coated Zr alloys is largely unexplored, except one study showing that a pre-oxidized ZrO₂ layer significantly enhances breakaway oxidation resistance of the fuel claddings.⁸³ Even though oxides should be thermodynamically stable (note that volatilization could occur) and act as diffusion barriers at elevated temperatures, additional validation of their physical integrity during oxidation is required.

Oxidation resistance of *polycrystalline diamond* coated cladding was slightly improved at 950°C.⁷⁷ Since carbon/carbon composites form gaseous carbon oxides during high-temperature oxidation, and substantial effort has been devoted to develop protective coatings for this category of materials,¹⁵⁵ the enhanced oxidation resistance of diamond coatings is expected to work only at low temperatures.

SiC coatings with various concentrations of Si on zircaloy plates showed enhanced oxidation resistance at 900°C in steam attributed to oxidation of the Si component to form a silica layer.¹⁰⁵ Oxidation of Cr-based coatings (Cr and CrC, CrSiC) on the inner side of a Zr alloy tube deposited by DLI-MOCVD revealed that amorphous chromium carbide coatings (up to ~25 µm thick) showed the most promising properties.^{20,21} The CrC coatings demonstrated good adherence, preserving their integrity after oxidation at 1100°C followed by water quenching. However, some small cracks were evident. In addition, the coatings shifted the catastrophic oxidation of the uncoated alloy substrate towards higher temperatures and delayed its complete oxidation for more than 2 h at 1200°C in steam. Oxidation of PVD ZrAlC coatings on a Zr alloy substrate indicated no protection effect at temperatures beyond 800°C in steam owing to cracking and formation of a mixed oxide scale (ZrO₂ and Al₂O₃).¹⁰⁷

Improving the oxidation resistance of *transition metal nitride* (TMN)-based coatings has represented an important topic for many decades with the purpose of increasing the durability and efficiency of cutting tools.¹⁵⁶ Hard TiN protective coatings were initially developed for industrial usage. Their limited oxidation resistance has motivated the continuous evolution toward ternary and quaternary Al-containing TMN (such as TiAlN, CrAlN and CrAlYN) systems with enhanced oxidation performance as well as additional attractive mechanical and chemical properties.^{156,157} Mixed oxide scales consisting of both Al₂O₃ and transition metal oxide grow during high-temperature oxidation of these Al-containing nitride coatings. Therefore, CrAlN-based coatings, forming a mixed Cr₂O₃ and Al₂O₃ scale, typically possess better oxidation resistance than TiAlN-based coatings. The incorporation of minor amounts of “reactive” elements (for example Y, Hf, Zr, Yb) can further reduce the oxidation rate and improve scale adherence.¹⁵⁶ Brova *et al.* have investigated the oxidation performance of un-doped and ytterbium-doped titanium aluminum nitride (TiAlN, Ti:Al ~ 1) coatings on Zr alloys.¹¹⁴ Fig. 19 shows the microstructure of the oxide scale after oxidation at 1000°C for 25 min in air. The coated samples clearly demonstrated improved oxidation resistance at this temperature, with roughly eight times thinner oxide layer on top. Logically, the oxide scale on coatings are composed of both TiO₂ and Al₂O₃, Fig. 19(b) and (c). However, a large quantity of fine voids was found inside the oxide layer and partial delamination likely occurred at the scale/coating interface. This suggests that an optimized Yb dopant concentration leads to a lower growth rate of oxide scale and improved scale adherence, Fig. 19(c). Over-doping of Yb will impose adverse effects and worsen the oxidation resistance. Validation of coating performance at higher temperature in a steam atmosphere is needed.

Enhanced oxidation performance was also confirmed for other nitride coatings, for instance CrN, CrAlN, TiAlCrN and CrAlSiN, on Zr alloy substrates during oxidation up to at least 1200°C in an air or steam atmosphere.^{41,112,115,158,159} However, one common issue for these hard nitride coatings is that they are susceptible to cracking especially undergoing temperature changes and/or high deformation. One example is shown in Fig. 20. The rapid growth of Zr oxides beneath the localized cracked coatings can exacerbate the premature failure of the coatings during oxidation.

Alumina-forming MAX phases (Ti₂AlC, Ti₃AlC₂ and Cr₂AlC) possess excellent high-temperature oxidation resistance and autonomous self-healing capability,^{122,160} making them exceedingly promising candidates as protective coatings. The oxidation performance of Ti₂AlC and Cr₂AlC coatings on Zr alloy substrates has been reported. During high-temperature oxidation, thick Ti₂AlC coatings deposited by spraying often cannot establish a dense and continuous alumina layer on top due to their porous structure and many impurities.¹¹⁷ In the case of thin Ti₂AlC coatings deposited by PVD, improved oxidation resistance was shown at the relatively low temperature of 800°C in steam. However, rapid oxidation with significant cracking and spallation of the coatings occurred once oxidation temperatures reached 1000°C.¹²⁰ Growth of layered, mixed oxide scales likely caused the poor performance at elevated temperatures. In comparison, thin Cr₂AlC coatings possess superior oxidation resistance and oxidation-induced self-healing capability via growth of a thin and dense alumina layer during oxidation at 1000°C in steam.⁸⁷ Fig. 21

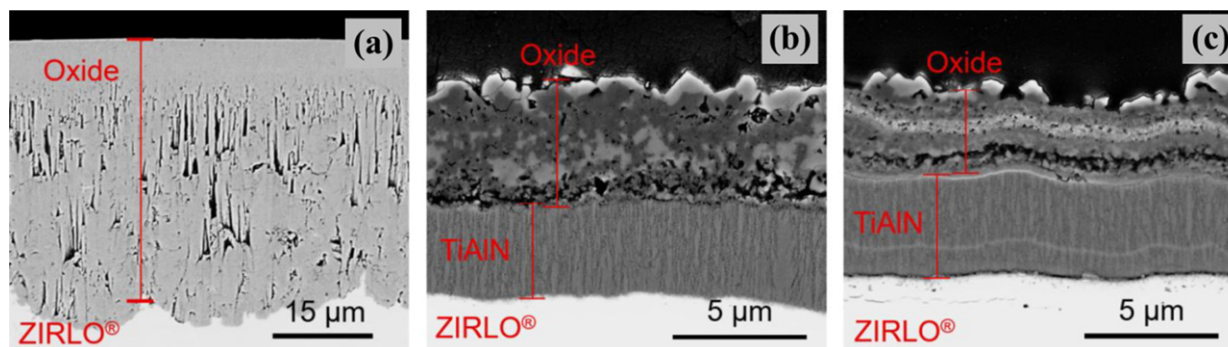


Fig. 19 Cross-sectional SEM-BSE images after oxidation at 1000°C for 25 min, (a) uncoated Zr alloy, (b) TiAlN coated and (c) TiAlN with 0.64 at% Yb coated. Reproduced from Pauley, M.A., Motta, A.T., Alati, E., *et al.*, 2017. *Surf. Coat. Technol.* 331, 163–171.

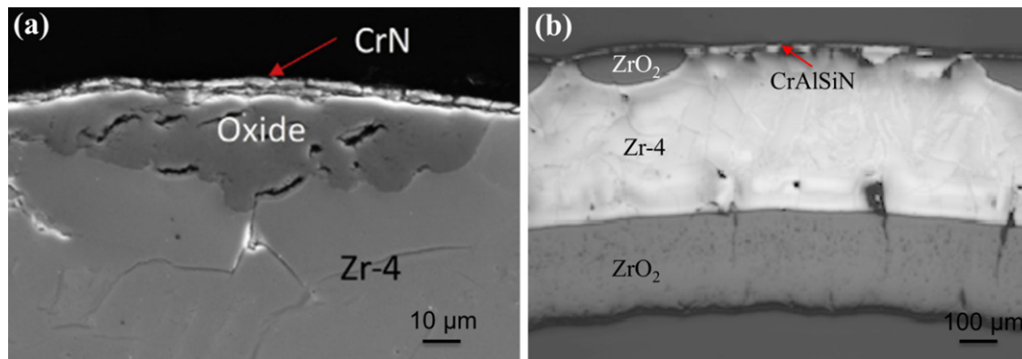


Fig. 20 Cross-sectional images of (a) CrN coating and (b) CrAlSiN coating oxidized at 1100°C in steam for 15 min and 30 min, respectively. Cracking of both coatings with rapid growth of ZrO_2 layer beneath cracks was observed. Reproduced from Daub, K., Van Nieuwenhove, R., Nordin, H., 2015. *J. Nucl. Mater.* 467, 260–270. Skarohlid, J., Skoda, R., 2017. High temperature behaviour of CrAlSiN MAX phase coatings on zirconium alloy. In: *Proceedings of the 2017 Water Reactor Fuel Performance Meeting*, pp. 1–5. Jeju Island, Korea.

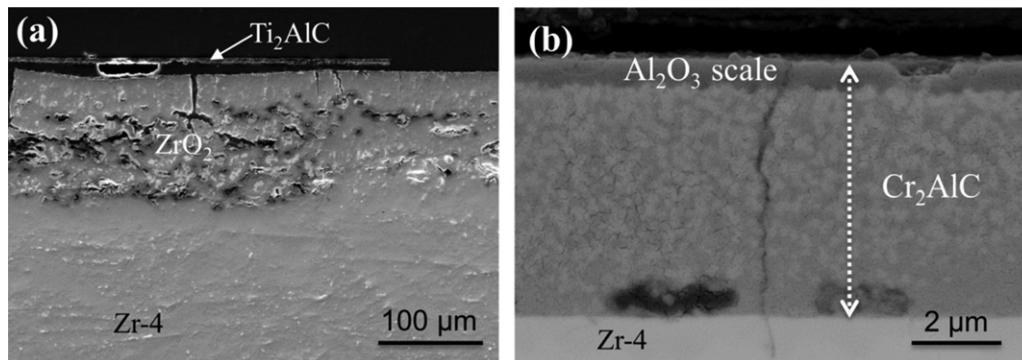


Fig. 21 Cross-sectional images of (a) Ti_2AlC coated and (b) Cr_2AlC coated Zr alloy after oxidation at 1000°C in steam for 5 min and 60 min, respectively. Reproduced from Tang, C., Steinbrueck, M., Stueber, M., *et al.*, 2018. *Corros. Sci.* 135, 87–98. Tang, C., Steinbrueck, M., Grosse, M., *et al.*, 2018. Improvement of the high-temperature oxidation resistance of Zr alloy cladding by surface modification with aluminum-containing ternary carbide coatings. In: *Proceedings of the International Congress on Advances in Nuclear Power Plants*, pp. 694–700. Charlotte, USA.

illustrates the microstructure of Ti_2AlC and Cr_2AlC coated Zr alloys via PVD after oxidation at 1000°C in steam. A thick ZrO_2 layer formed on the Ti_2AlC coated sample even after oxidation for just 5 min. A protective alumina layer, $\sim 0.6 \mu\text{m}$ thick (two hundred times thinner than that of ZrO_2 layer formed on uncoated alloy), formed on the Cr_2AlC coating after oxidation for 60 min, **Fig. 21(b)**. An initial micro-crack within the coating was healed via fast growth of alumina and associated volume expansion. However, during oxidation, rapid diffusion of Al from the MAX phase coatings into the substrate takes place because of the high migration rate of the A-element in the MAX phase structures.

4.17.5.1.3 Multilayer coatings

Investigations performed to evaluate the oxidation performance of multilayer coatings on Zr alloys mainly focused on verifying the capability of a diffusion barrier to prevent inter-diffusion at elevated temperatures.

Stoichiometric CrN was evaluated as a diffusion barrier for metallic Cr coatings.⁴¹ A thin CrN layer was ineffective at elevated temperatures because of a phase transformation (from CrN to $\text{Cr}_2\text{N} + \text{N}_2$ induced by inward diffusion of N) and concomitant cracking. A thick CrN layer (13 μm) demonstrated satisfactory performance, which prohibited Cr-diffusion into the substrate and Cr-Zr melting above 1350°C during exposure in steam for a short period (2 min). Additionally, inward diffusion of nitrogen resulted in formation of a thin stable ZrN layer at the coating/substrate interface.

A thin TiC interlayer has been proposed as a diffusion barrier between Ti_2AlC coatings and Zr alloy substrates.¹²⁰ The TiC barrier can suppress the rapid inward diffusion of Al into the substrate at 800°C; however, the coating system failed at elevated temperatures in steam owing to their low oxidation resistance.

Both $\text{Mo}^{28,50,64,154}$ and ZrO_2 ⁸² have been examined as a buffer layer for FeCrAl coatings. Negligible inter-diffusion between the coating and substrate was seen during oxidation to 1200°C. **Fig. 22** compares the oxidation performance of coatings with and without a diffusion barrier. The oxidation rate of a single-layer FeCrAl coated specimen was even faster than an uncoated one at 1000°C in steam owing to Fe-Zr eutectic reaction, **Fig. 22(a)**. Significantly reduced oxidation kinetics was observed after applying a

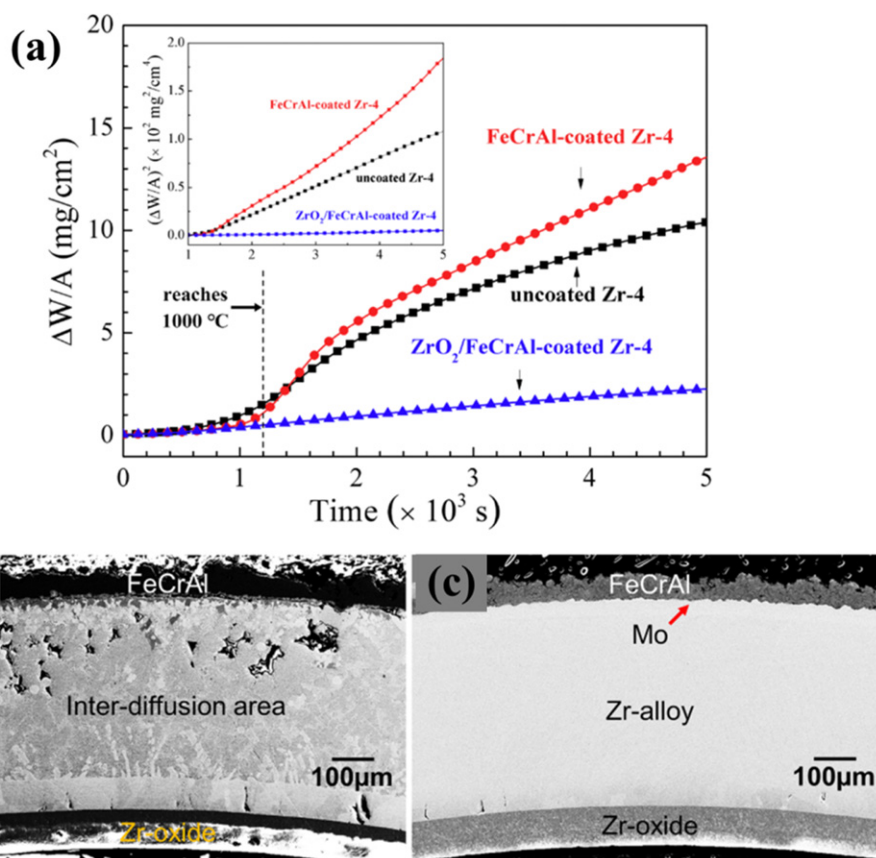


Fig. 22 Comparison of oxidation rate and microstructure of FeCrAl coatings on Zr alloy substrate without and with diffusion barrier. (a) Oxidation rate at 1000°C in steam without or with ZrO₂ interlayer, cross-sectional images after oxidation at 1200°C in air for 20 min (b) without and (c) with Mo interlayer. Reproduced from Wang, Y., Tang, H., Han, X., *et al.*, 2018. *Surf. Coat. Technol.* 349, 807–815. Maier, B., Yeom, H., Johnson, G., *et al.*, 2018. *JOM*, 70, 198–202.

ZrO₂ buffer layer synthesized by plasma electrolytic oxidation.⁸² As seen in Fig. 22(b), the alloying elements in the cold-sprayed FeCrAl coating penetrated the whole cladding tube tested in air at 1200°C for 20 min. Under identical conditions, a Mo buffer layer with around 20 μm thickness successfully suppressed the inter-diffusion between the FeCrAl coating and Zr alloy substrate.⁵⁰ The eutectic reaction temperatures of Zr-Mo and Fe-Mo¹⁶¹ are at 1550°C and 1450°C, both considerably higher than that of Zr-Fe (~930°C, Fig. 17).

4.17.5.2 Severe Accidents

Only a few studies have been dedicated to understanding the protective effect and failure mechanisms of various coating-substrate systems under simulated severe accident scenarios. The available data are largely regarding Cr-based coatings (like metallic Cr, CrN and Cr₂AlC MAX phase). The principal degradation mechanisms, except oxidation failure, identified with respect to metallic coatings and ceramic coatings during severe accidents (beyond 1200°C) are the formation of a liquid phase via eutectic reaction and brittle cracking, respectively.

Metallic Cr coatings reveal the capability to prevent the Zr alloy substrates from rapid oxidation and oxygen ingress up to 1300°C in steam, depending on coating thickness.⁵⁴ At temperatures above the Zr-Cr eutectic temperature (~1330°C), formation of liquid phase accompanied by its continuous displacement triggers rapid failure of the coated cladding. Accelerated Cr interaction with Zr alloy substrates drives the chromium into the inner regions of the cladding corresponding to the prior β-Zr phase owing to oxygen diffusion. Brachet *et al.* observed a fairly homogeneous and uniform ZrO₂ layer on the Cr coated cladding after being tested to 1450°C (100 s) in steam, even though the surface became convoluted with many protrusions and blisters. The authors suggested that formation of a liquid Zr-Cr phase might not drastically modify the oxidation mechanisms and kinetics of the Zr alloy cladding in high-temperature steam environment.⁴³ On the other hand, a slightly thicker ZrO₂ layer and higher oxidation rate of the Cr coated surface was also reported relative to the un-coated surface at 1400°C (2 min) in steam.⁴⁸ Transient oxidation of a cold-sprayed Cr coated cladding tubes up to 1500°C in steam resulted in accelerated hydrogen release rate once the temperature exceeded the Cr-Zr eutectic temperature. Subsequently, the

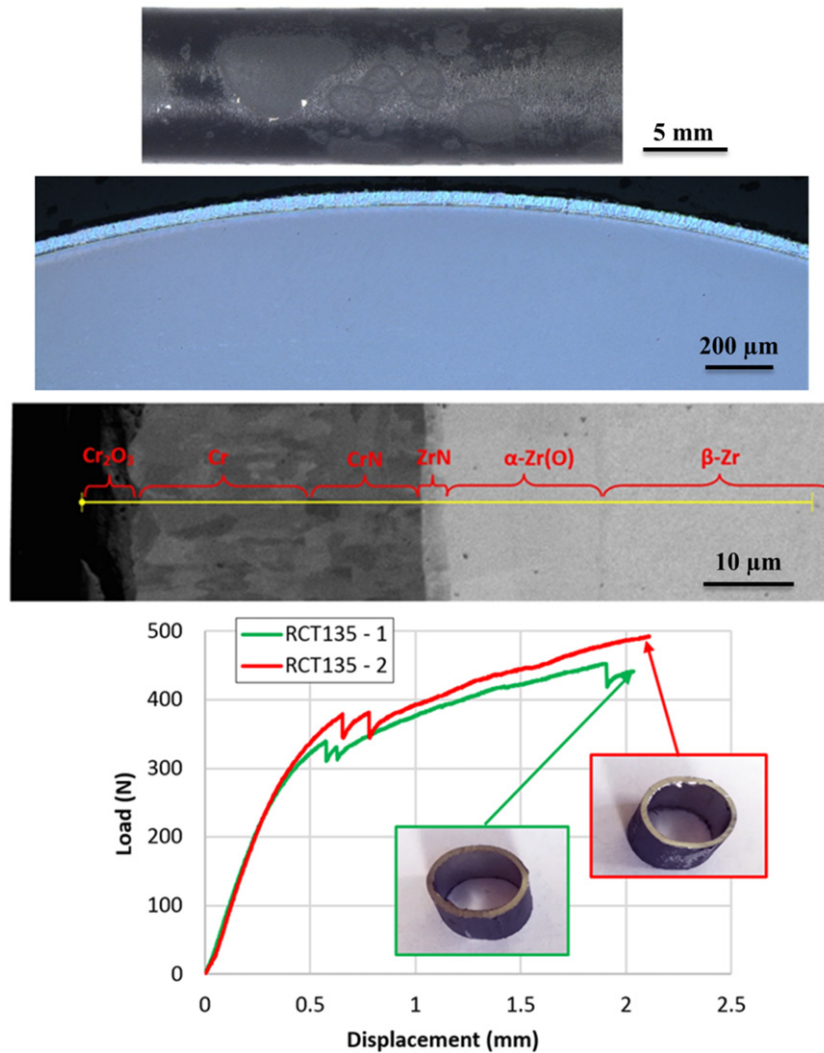


Fig. 23 Appearance, microstructure and ring compression of thick CrN/Cr (13/25 μm) coated Zr alloy after oxidation at 1365°C for 2 min in steam. Reproduced from Krejci, J., Ševeček, M., Kabátová, J., *et al.*, 2018. Experimental behavior of chromium-based coatings. In: Proceedings of the TopFuel pp. 1–14. Prague, Czech Republic.

hydrogen release rate increased steeply at temperatures above $\sim 1450^\circ\text{C}$ and surpassed that of the uncoated reference Zircaloy-4, indicating a considerably faster oxidation rate.⁵²

Krejci *et al.* have tested single-layer sub-stoichiometric $\text{Cr}_{90}\text{N}_{10}$ coatings and two bilayer coatings: thin CrN/Cr (3/19 μm) and thick CrN/Cr (13/25 μm) on Zr alloys in steam above the Cr-Zr eutectic temperature.⁴⁸ Failure of the single-layer $\text{Cr}_{90}\text{N}_{10}$ and the thin CrN/Cr coated surfaces with melting plus a thicker oxide layer was seen after testing at 1400°C in steam for 2 min. The thick CrN/Cr multilayer coatings survived at 1365°C in steam for 2 min without coating-substrate melting, coating spallation or local coating failures, as shown in Fig. 23. A thin ZrN layer formed at the coating/substrate interface, preventing diffusion of chromium into the Zr alloy substrate. Oxygen penetrated the coating layer, forming an $\alpha\text{-Zr(O)}$ layer underneath the coatings. The oxidized specimen moreover demonstrated a high residual ductility during ring compression tests. These promising results motivated the authors to develop functional gradient coatings based on Cr and CrN for the ATF application.

Fig. 24 compares the hydrogen release rate and the oxide layer thickness of thin Cr_2AlC coated (6 μm) and uncoated Zircaloy-4 from a transient oxidation test heating from 500°C to 1400°C in steam. As concluded from Fig. 24(a) and (c), the coatings cracked at $\sim 1260^\circ\text{C}$. After coating cracking the hydrogen release rate increased abruptly and the oxidation rate of the coated sample surpassed the uncoated one at around 1300°C . An inhomogeneous oxide layer was observed after testing, with a thicker layer beneath the cracks on the coated sample. However, there was no apparent evidence indicating liquid phase formation between the coating layer and the Zr alloy substrate after testing. Selective oxidation of Al in Cr_2AlC coatings typically leaves a Cr-C layer beneath, which probably increased the eutectic reaction temperature of the system.¹⁶²

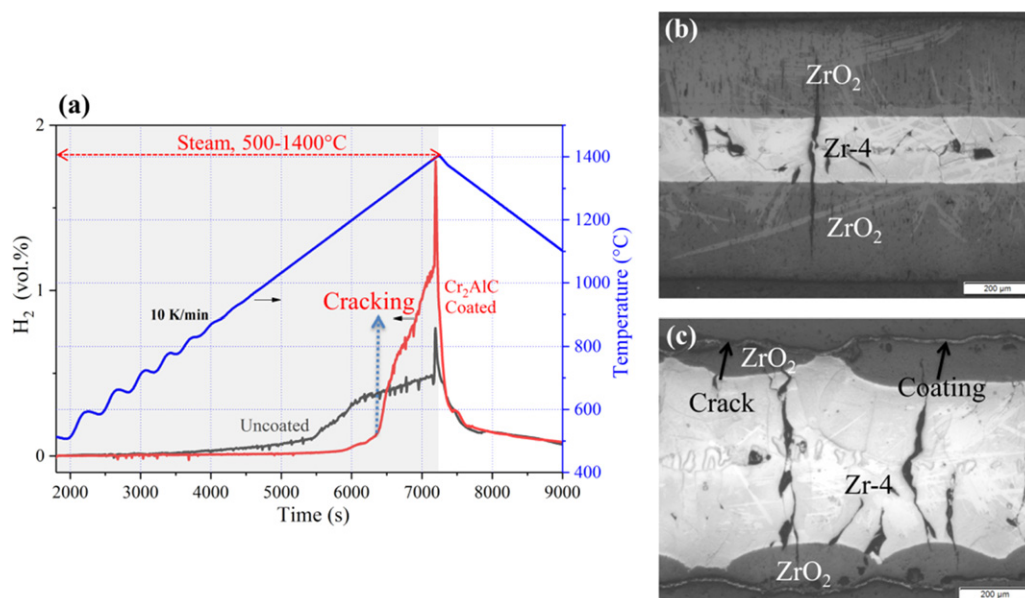


Fig. 24 (a) Hydrogen release rate of a transient test from 500°C to 1400°C in steam and cross-sectional SEM images of (b) uncoated and (c) Cr₂AlC coated Zircaloy-4 after testing.

4.17.6 Conclusion and Outlook

Surface modification of state-of-the-art zirconium-based alloy fuel claddings with innovative high-temperature oxidation/corrosion resistant metallic or ceramic coatings are being intensively pursued for enhanced accident tolerant fuel cladding applications. This approach represents a near-term evolutionary strategy and allows for an easier licensing pathway compared to alternative cladding materials.

A variety of materials have been proposed and examined and the principal coating concepts comprise metallic coatings, ceramic coatings and multilayer coatings. Multilayer coating designs are anticipated to overcome or alleviate the limitations of single-layer metallic (high interdiffusion rate and low eutectic reaction temperature with underlying Zr alloy substrate) and ceramic (low fracture toughness) coatings. Cr-based coatings (for instance pure Cr, CrN and Cr₂AlC) represent some of the most attractive and promising options considering their satisfactory performances under both normal and accident conditions.

The nature and performance of the coated claddings are highly affected by the constituent and microstructure of the coating-substrate system, which depends on the applied fabrication technology and concurrent processing parameters. Physical vapor deposition and cold spraying are the two prevalent coating methods for coated ATF application. The typically low deposition temperature and thin coating thickness via PVD processing are favored because of the negligible impact on microstructure modification of the substrate and neutronic economy. Thick coatings can be straightforwardly achieved via spraying processes. However, compositional, structural and mechanical inhomogeneities for sprayed coating-substrate systems have been frequently seen.

The specific application characteristics of enhanced ATF claddings require the coating materials to resist hydrothermal corrosion (normal operation) and high-temperature steam/air oxidation (accident scenarios). Both working environments require growth of a thermodynamically stable and protective oxide layer that acts as an effective diffusion barrier. The robust oxide scales that can endure at elevated temperatures in oxidizing atmosphere (accident scenarios) are those made of chromia, alumina or silica. The fast growth rate of Cr₂O₃ scale accompanied by formation of volatile hydroxides at elevated temperatures generally restricts its application to lower temperatures (ca. 1300°C). However, Al₂O₃ and SiO₂ are unstable via formation of soluble aqueous ions under normal operation conditions. Si- and Al-containing coatings often experience rapid hydrothermal dissolution or selective leaching of these two elements (or oxides) during autoclave testing.

The structural integrity of the coating-substrate system obviously will be highly challenged in the reactor core due to various stresses, irradiation damage and, during accident scenarios, by rapid degradation (like ballooning and burst) of the fuel cladding substrate. Ideally, the coating should be highly adherent under a variety of working conditions or self-healing after defects have occurred. Pure Cr coated claddings display satisfactory performances under out-of-pile irradiation testing and one cycle in-pile testing. Ceramic coatings are vulnerable to cracking and spallation owing to their brittle characteristics and low toughness. During design-basis and/or severe accident conditions, the principal degradation mechanisms, except oxidation failure, identified with respect to metallic coatings and ceramic coatings are the formation of liquid phases via eutectic reaction and brittle cracking, respectively.

Numerous coating concepts have been proposed as enhanced ATF claddings and the majority of studies to date mainly focus on testing and verifying their feasibility under out-of-pile conditions in case of hydrothermal corrosion and/or high-temperature

oxidation. A comprehensive assessment and qualification of the coating-substrate system under long-term in-pile and (severe) accident conditions are required. Many knowledge gaps still exist, for instance the irradiation performance especially the chemical and physical stability of interfaces, mechanical behavior and degradation mechanisms under various situations. In addition, standard test methods and new failure criteria are needed to allow various coating concepts to be easily assessed and their applicability validated.

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See also: 4.02 Water Chemistry Control in LWRs. 4.03 Corrosion of Zirconium Alloys. 4.15 Steam Oxidation in Accident Conditions. 6.09 Ceramic Coatings for Fusion Reactors.

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