Review

Recent Advances in Protective Coatings for Accident Tolerant Zr-Based Fuel Claddings

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Abstract: Zirconium-based alloys have served the nuclear industry for several decades due to their acceptable properties for nuclear cores of light water reactors (LWRs). However, severe accidents in LWRs have directed research and development of accident tolerant fuel (ATF) concepts that aim to improve nuclear fuel safety during normal operation, operational transients and possible accident scenarios. This review introduces the latest results in the development of protective coatings for ATF claddings based on Zr alloys, involving their behavior under normal and accident conditions in LWRs. Great attention has been paid to the protection and oxidation mechanisms of coated claddings, as well as to the mutual interdiffusion between coatings and zirconium alloys. An overview of recent developments in barrier coatings is introduced, and possible barrier layers and structure designs for suppressing mutual diffusion are proposed.

Keywords: protective coatings; high temperature oxidation; corrosion; fuel claddings; zirconium-based alloys; accident tolerant fuel; interdiffusion; barrier layers

1. Introduction

In recent decades, zirconium-based alloys have been used in the nuclear industry as the main material for fuel claddings and other structural components of pressurized and boiling water reactors (PWRs and BWRs), Russian water–water energetic reactors (VVERs) and high-power channel-type reactors (RBMK) [1]. During normal operation, zirconium alloys form a protective zirconium oxide layer that reduces cladding corrosion in the coolant. The key factors affecting claddings degradation are radiation swelling and embrittlement caused by oxidation and hydrogenation of the zirconium claddings [2–4]. However, zirconium alloys demonstrate poor oxidation kinetics at elevated temperatures. Since 2011, following the tragic Fukushima Daiichi Nuclear accident, great attention has been devoted to the development of a new concept of nuclear fuel to improve the safety of nuclear reactors during normal operation, transient modes and under accident conditions [5–10]. A concept called “accident tolerant fuel (ATF)” indicates a strategy to prevent/limit the interaction of cladding material with water steam, or hydrogen embrittlement, and to reduce heat generation during cladding oxidation and increase “processing time” under accident conditions before re-flooding of the nuclear core [9,11,12].

The most crucial conditions for fuel claddings can occur in the case of a loss of coolant accident (LOCA) [1,10]. LOCA events can be caused by a breakup of the primary cooling system that results in the loss of pressure in the nuclear core and vaporization of the coolant. Under these conditions, the fuel temperature rises, thereby increasing the porosity of
the fuel and resulting in its fragmentation. The fuel cladding temperature also increases abruptly. When Zr-based (E110, E635, Zircalloys, M5, ZIRLO, etc.) claddings interact with water steam at a high temperature (above 800 °C), it causes oxidation and embrittlement by releasing additional heat due to the exothermic reaction:

$$\text{Zr} + 2\text{H}_{2}\text{O} = \text{ZrO}_2 + 2\text{H}_2\uparrow, \Delta H = -584.5 \text{ kJ/mol at } 1200 ^\circ \text{C}$$ (1)

Therefore, the development of ATF cladding material is desperately needed to enhance the robustness of LWRs in normal and possible accident conditions.

Nowadays, two main ATF strategies are considered. The first is to replace current cladding material with SiC/SiC composites [13–16], FeCrAl [17–121], molybdenum alloys [20,22–25] or Ni-based stainless steels [26]. Taking into account the duration and possible total costs for developing a new type of cladding material, this way is considered as a long-term strategy. The second ATF concept is the development of protective coatings on the surface of Zr fuel claddings [27,28]. Protective coatings should strongly improve corrosion and high-temperature (HT) oxidation resistance, wear-resistance and reduce hydrogen absorption of Zr-based alloys used in LWRs. Therefore, coating technology can be added to the technological process of nuclear fuel production that can be achieved in a short-term period. Despite the simplicity of this approach, a large number of possible factors (coating adhesion, thermal conductivity, thermal neutron cross-section, radiation resistance, mechanical properties [29]) can affect the behavior of coated Zr claddings in both normal and accident conditions. Currently, numerous studies are being performed to improve zirconium alloy performance by the deposition of metallic (Fe-based alloys, Cr, Cr-Al, Y, Ni-Cr, etc.), non-metallic (oxides, nitrides, carbides) or MAX-phase coatings [19,30–32]. Among a variety of coatings, the highest performance in LOCA scenarios belongs to materials which can produce oxide phases such as alumina, zirconia, chromia or silica [33–36].

This review emphasizes recent advances in protective coatings for ATF zirconium claddings. Section 2 introduces the Zr-based alloys and their behavior under normal and accident conditions. Section 3 presents different types of protective coatings for ATF concepts, while Section 4 elaborates on the mechanism of protection of selected coating types and provides several suggestions to develop Zr-based ATF claddings.

2. Zirconium-Based Alloys

Zirconium-based alloys have gained commercial acceptance based on their excellent properties and availability of metal in sufficient reserves and obtainable costs. Zirconium-alloy clad tubes were first developed by the United States Navy Nuclear Propulsion Program in the 1950s [36,37]. Nuclear-grade Zr-alloys consist of more than 95 percent Zr, and therefore possess characteristics close to those of pure Zr. Over decades, by optimization of elemental composition, the USA favored the Zr-Sn based alloy system while Russia, Canada and other countries developed an Zr-Nb based alloy system [10,38,39]. Zircalloys, ZIRLO, E-grades and M5 alloys will be discussed in this section considering their material composition and oxidation performance under accident conditions.

2.1. Zr-Sn and Zr-Nb Alloys

Unalloyed zirconium has poor corrosion resistance, resulting in high stresses and cracking of zirconium oxide and its spallation [40]. To decrease its corrosion rate under the normal operation conditions of a nuclear reactor, additional dopants were added into Zr, which should not strongly influence the neutron economy. Today, Zr is mainly alloyed with Sn and Nb. Moreover, O, Cr, Fe and Ni are also added in Zr alloys to improve their mechanical and functional properties. Table 1 presents various compositions of cladding materials currently used in the nuclear industry.
Table 1. Composition of Zirconium-alloys (wt.%) [41–46].

| Alloys      | Sn  | Fe  | Cr  | Ni  | Nb  |
|-------------|-----|-----|-----|-----|-----|
| Zircaloy-2  | 1.50| 0.12| 0.10| 0.05| –   |
| Zircaloy-4  | 1.50| 0.20| 0.10| –   | –   |
| ZIRLO       | 1.02| 0.10| –   | –   | 1.01|
| OPT-ZIRLO   | 0.66| 0.11| –   | –   | 1.04|
| M5          | –   | 0.05| 0.015| –   | 1.0 |
| E110        | –   | –   | –   | –   | 0.95–1.05|
| E110 opt.   | –   | 0.025–0.07| –   | –   | 0.90–1.10|
| E110M       | –   | 0.07–0.15| –   | –   | 0.90–1.10|
| E125        | –   | –   | –   | –   | 2.20–2.60|
| E125 opt.   | –   | 0.025–0.05| –   | –   | 2.40–2.70|
| E635        | 1.1–1.3| 0.30–0.40| –   | –   | 2.40–1.05|
| E635M       | 0.70–0.90| 0.30–0.40| –   | –   | 0.70–0.90|

Zircaloy 2 (Zry-2) belongs to the Zr-Sn system that shows a good balance between corrosion resistance and mechanical properties. The addition of Fe, Cr and Ni dopants improves the oxidation resistance of Zry-2 alloy. However, the presence of Ni caused high hydrogen uptake, so Zircaloy-4 (Zry-4) without Ni and increased Fe content was developed. Nowadays, two type of Zircaloyes are used in the nuclear industry: Zry-2 in BWRs and Zry-4 in PWRs [41].

E110, E125 and E635 alloys belong to the Zr-Nb system used for structural components (fuel cladding, guide tubes, spacer grids, etc.) in the Russian VVER and RBMK reactors. These materials were developed from 1958 to 1971 and gained commercial acceptance in the 1980s, coupled with subsequent optimizations of their elemental compositions [45,46]. Despite the fact that both E110 and E635 alloys have been developed to possess creep resistance, high strength and resistance to irradiation growth, the E110 alloy has superior corrosion resistance in PWRs, while E635 provides high strength, resistance to creep and irradiation growth in BWRs [47,48]. E125 alloy is usually used for shroud pressure pipes of VVER and RBMK. E-series alloys are more vulnerable to breakaway corrosion than Zry-4, which results in higher oxidation rate and hydrogen uptake [7,49]. Thus, optimized modifications, such as E110opt., E110M, E125opt. and E635M, with Fe and O dopants, were developed to guarantee absolute assurance and integrity for use in the future generation of VVER (VVER-1200), which will operate at higher fuel burn-up [50,51].

ZIRLO alloy was designed by Westinghouse for PWR’s fuel claddings. This alloy includes dopants of Sn, Fe, Nb and O. In 2004, an optimized version of the alloy (OPT ZIRLO) with reduced Sn (0.66 wt.%) and similar Fe (0.10 wt.%–0.11 wt.%) content was designed. OPT ZIRLO alloy has higher corrosion and creep resistance compared with ZIRLO, especially in Li-containing media [52].

M5 alloy has been in a commercial application since the 1990s as base material of the fuel claddings for PWRs. M5 and E110 alloys have similar basic compositions of Zr-1%Nb with controlled content of other dopants. The absence of Sn and an optimized heat treatment process of M5 alloy production result in very good corrosion resistance and mechanical properties under high temperature and irradiation conditions [53–55].

2.2. HT Oxidation Behavior of Zr-Based Alloys

LOCA, or reactivity-initiated accidents, can result in rapid oxidation of zirconium claddings, overheating and depressurization due to exothermic oxidation reaction (1). To estimate oxidation behavior of Zr alloys at HT, several experiments simulating severe accidents were performed. The results of these tests are presented below.
Malgin et al. studied HT (900–1250 °C) oxidation behavior of E110opt and E110M sponge-based Zr alloys in water steam [56]. The obtained results show similar oxidation kinetics of both alloys without breakaway effects. Yan et al. showed that the oxidation kinetics of sponge-based E110 alloy accelerates with increasing temperature, and a good correlation with the Cathcart–Pawel prediction model [57] was observed at 1200 °C (Figure 1) [58]. The equivalent cladding reacted (ECR) parameter up to 17% of the initial cladding thickness was reached after 220–230 s at 1200 °C. Exceeding this value leads to a significant degradation of the mechanical properties of the fuel claddings, according to the criteria of the US Nuclear Regulatory Commission (NRC) [59].

Le Saux et al. studied the breakaway oxidation of Zry-4 and M5 (Framatome) alloys in flowing steam at 950–1050 °C, as shown in Figure 2 [60]. The results concluded that the higher the temperature was, the greater the weight gain at which Zry-4 breakaway oxidation occurred in the ranges 8–11, 13–14 and 25–34 mg/cm², at 950–975, 1000 and 1025 °C, respectively. In contrast, M5 (Framatome) oxidized from both sides did not exhibit breakaway oxidation at temperatures from 950 to 1050 °C for up to 250 min (15,000 s). However, M5 breakaway oxidation occurred at 1025 °C beyond 15,000 s, with a weight gain of 15 mg/cm².

Steinbrueck et al. performed isothermal oxidation tests on Zry-4 alloy in a mixture of steam–nitrogen atmosphere by varying the volume fraction of the supplying gases at 600–1200 °C [61]. It was revealed that nitrogen significantly affected the oxidation kinetics due to formation and re-oxidation of ZrN to ZrO₂ near the metal/oxide interface. The re-oxidation process results in the loss of protective oxide scale due to the formation of microcracks as a result of high-volume expansion (approx. 48%) [62]. Thus, it is necessary to consider the effect of nitrogen, as it leads to the degradation of mechanical properties of zirconium alloy claddings and significantly increases oxidation kinetics and, therefore, the generation of hydrogen under accident conditions [63].

Since these results demonstrate low resistance of Zr-based alloys to HT oxidation under accident conditions, a new concept of nuclear material was developed to improve the safety of nuclear reactors [9].
3. Protective Coatings for ATF Claddings

Numerous studies have been performed to improve zirconium alloys’ performance under both normal and accident conditions by the deposition of protective coatings [64–67]. Coated Zr alloys show enhanced corrosion and HT oxidation resistance; although reduced, relatively thin coatings are not influenced by the thermomechanical behavior of Zr-based claddings [73], the coatings should not noticeably change neutron absorption in LWRs [74] and heat transfer between the cladding and coolant [75].

Most published papers and reviews showed that ATF coatings should have at least one of Cr, Al or Si in their composition in order to enable the formation of a protective scale (Cr₂O₃, Al₂O₃, or SiO₂) [21,76–79]. Section 3 highlights recent developments in protective coatings for Zr-based alloys. A summary of the selected coatings and their performance under normal operational and accidental conditions is presented in Table 2.

3.1. Metallic Coatings on Zr-Based Alloys

3.1.1. Fe-Based Coatings

Currently, there are two major research institutes focusing on the development of FeCrAl coatings for nuclear fuel claddings. These are the Korea Atomic Energy Research Institute (KAERI) and the University of Illinois Urbana-Champaign (UIUC). Fe-based coatings on Zr necessitate a barrier layer between the coating and substrate to mitigate Zr-Fe eutectic formation at high temperatures [80]. Zhong et al. investigated the oxidation performance of FeCrAl coatings under HT steam conditions [81]. In this study, FeCrAl was deposited on Zry-2 alloy using magnetron sputtering. Based on the experimental results, 1 µm-thick FeCrAl coating prevented the oxidation of the Zry-2 substrate in steam at 700 °C up to 15 h, while a thin FeCrAl (0.3 µm) film did not protect the alloy. Furthermore, investigations performed under autoclave testing (20 days) in a simulated BWR environment demonstrated an adequate performance without the loss of coating integrity. Kim et al. investigated the surface-modified Zr cladding concept: an outer FeCrAl protective layer was chosen as a coating to enhance the oxidation/corrosion resistance of Zr alloy deposited by laser coating and arc ion implantation methods to increase the adhesion strength of the coating and the Zr alloy tubes [82]. The obtained samples demonstrate improved corrosion/oxidation performance, creep and irradiation resistance compared to commercial Zr claddings. Good radiation resistance was also observed for FeCrAl alloys.
under heavy ion irradiation [83]. There was no void formation or Cr-enriched phases in 10Cr and 13Cr FeCrAl alloys, and irradiation-induced defects only contributed to hardening. Dabney et al. showed that thick FeCrAl coatings obtained by cold spraying demonstrate high oxidation resistance during autoclave tests and HT oxidation in the air [84]. However, a fast diffusion of Fe from FeCrAl coating to Zr alloys caused a thick interlayer composed of (Fe,Cr)₂Zr, FeZr₃ and FeZr₂ Laves phases (Figure 3a,b) [85].

Park et al. investigated FeCrAl coatings deposited onto Zr substrates using cold spraying techniques [86]. For the FeCrAl/Zr system, a Mo layer was deposited between the FeCrAl coating and the Zr substrate to inhibit interdiffusion at high temperatures. As a result of mutual diffusion in the FeCrAl/Mo/Zr system, a complex multilayer structure was formed (Figure 3c,d). The FeCrAl coatings improved the oxidation resistance of the Zr alloy when exposed to a steam environment at 1200 °C. The ballooning behavior and mechanical properties of the coated samples studied under simulated LOCA conditions revealed higher burst temperatures, lower circumferential strain and smaller ruptures compared to the bare Zr. In addition, four-point bending and ring compression tests indicated a minimal increase in the maximum load and higher residual ductility of the coated Zr alloy, respectively [86].

3.1.2. Chromium-Based Coatings

Metallic Cr-based coatings are most promising in that they meet the basic requirements for ATF coating materials for fuel Zr claddings. Chromium has a high melting point, high corrosion resistance in water and steam due to a protective chromia scale, and a coefficient of thermal expansion similar to zirconium alloys. A wide variety of methods were implemented to deposit Cr coatings on Zr alloys such as magnetron sputtering [87].

Figure 3. Cross-section SEM images after 1200 °C air oxidation: (a) FeCrAl-coated Zircaloy-4 and (b) corresponding EDS line scan; (c) FeCrAl/Mo coating and (d) magnified image of the FeCrAl/Mo/Zr interface. Reproduced from [84] with permission by Elsevier.
cathodic arc deposition [88], cold spraying [89], 3D laser cladding [90], electroplating [91], etc. The high potential of these coatings is also confirmed by the involvement of large industrial/research institutes such as CEA (France), VNIINM (Russia), KIT (Germany) and others. Several full-scale tests with Cr-coated Zr claddings with UO₂ fuel in nuclear reactors are being performed at present.

Good protective properties of Cr coatings were demonstrated under normal operation conditions: autoclave testing in PWR and BWR simulated medium [65–67,92]. Wei et al. showed high corrosion resistance in Cr-coated Zry-4 alloy in both H₂BO₃-LiOH and dissolved oxygen containing water [67], showing only 50–100 nm stable Cr₂O₃ scale after a 3000 h autoclave test. Chromium coatings deposited on Zry-4 alloy exhibited promising performance under steady-state, power ramp and LOCA transient conditions [93,94]. Brachet et al. showed good protective properties of a 5–12 µm thick Cr coating under steam oxidation at 1200 °C (Figure 4) [87]. It was demonstrated that the coating enhanced the oxidation resistance of the alloy and ensured the integrity of the cladding for a longer oxidation time (approx. 10 times longer than current LOCA criteria). Ma et al. showed that Cr coatings could protect Zr-1Nb alloy from HT steam oxidation at 1200 and 1300 °C (Figure 5) [95]. It was shown that the thickness of the formed Cr₂O₃ and residual Cr layers depends on oxidation time, which is probably due to the combined effect of the ongoing redox reactions between chromium oxide and zirconium, also observed by Han et al. [96].

![Figure 4. Optical images and weight gain evolution of uncoated and Cr-coated (5–12 µm) Zry-4 alloy during steam oxidation at 1200 °C. Reproduced from [87] with permission by Elsevier.](image)

Results of mechanical tests under ambient and elevated (400 °C) temperatures showed no significant difference between the Cr-coated and the uncoated Zr claddings [65,90,97]. Kim et al. investigated the mechanical behavior of Zry-4 alloy with 3D laser-coated Cr coatings (80–120 µm) under ring compression and tensile tests [90]. The results indicate good adhesion and no defects in the Cr coatings up to 4% strain. The generation of cracks occurred at 6% strain without coating spallation or peeling. Ribis et al. analyzed the atomic-scale structure of the Cr/Zry-4 interface where the Cr coating was deposited using PVD method [98]. It was found that a thin layer of Laves Zr(Cr,Fe)₂ phase with C14 and C15 polytypes was formed at the interface, while the coherent boundaries ensured good adhesion of the coating.

The adhesion behavior of Cr coatings was also affected by oxidation and diffusion processes at the coating/alloy interface [72]. Jiang et al. performed a comparative analysis of cracking resistance of multi-arc ion plated Cr and CrN coatings on Zry-4 alloy under
It was revealed that Cr coatings exhibit a brittle-to-ductile transition under thermomechanical loading, which results in their better cracking resistance compared to CrN coatings.

Several studies presented a good radiation resistance of chromium coatings under ion irradiation [100–102]. The stabilization of C14 and disappearance of C15 polytypes in the Cr/Zry-4 samples due to continuous incoming Fe flux were found during 20 MeV Kr+ irradiation at 400 °C. Despite this, the samples retained their adhesion and microstructure stability after ion irradiation [100]. An acceptable swelling of ~1.6% was observed at an irradiation temperature of 500 °C under 1.4 MeV heavy ion radiation up to 25 dpa [101]. This is twice lower than the allowable swelling value (~5%) for reactor materials.

Cr-Al alloy coatings show better oxidation resistance than pure chromium [80,103,104]. However, a more complex and heterogeneous structure of the oxide layers forms after oxidation [105], which requires more detailed studies under long-term HT steam oxidation, as well as B-DBA conditions. Ni-Cr coatings exhibit better ductility than pure Cr coatings but, at high temperatures, they show lower oxidation resistance and rapid diffusion of Ni inside the zirconium alloy occurs [106,107].

**Figure 5.** Optical and SEM images of Cr-coated zirconium alloy cladding after high-temperature steam oxidation at 1200 °C for 0.5 h (a), 1 h (b), 2 h (c), 4 h (d), and 1300 °C for 0.5 h (e) and 1 h (f). Reproduced from [95].

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### 3.1.3. Yttrium-Based Coatings

The resistance of yttrium to oxidation, as well as the formation of stable protective yttrium oxides at very high temperatures, made it very attractive for study. Sridharan et al. investigated surface modified Y-coated Zry-2 alloy and observed a decrease in the oxidation rate in supercritical water at 400 °C for 7 days (168 h) [108]. Kim et al. investigated the surface modification of 2 mm-thick Zry-4 alloy by deposition of Y2O3 (10 µm) using a laser beam scan method to produce an oxide dispersion strengthening (ODS) treatment [109]. It has been shown that the yield strength of Zry-4 with the ODS layer was 65% higher compared to uncoated alloy at 500 °C, therefore enhancing high-temperature strength to defeat the ballooning behavior of fuel cladding during an accident event [110]. However, the limited research on these types of coatings does not allow us to confirm the feasibility of their use as ATF materials.
3.1.4. HEAs Coatings

High entropy alloys (HEA), also called multi-principal component alloys, are solid solutions of at least four elements in near equimolar ratios [111,112]. HEAs demonstrate a wide range of outstanding properties, such as high thermal stability, corrosion resistance and radiation damage tolerance [113,114]. Zhang et al. investigated corrosion behavior of a 3 µm-thick AlCrMoNbZr HEA coating deposited on an N36 alloy (Zr-1Sn-1Nb-0.3Fe) in static water at 360 °C and 18.7 MPa for 30 days [115]. It was reported that the oxidation resistance of the N36 alloy increased threefold due to multiphase oxide phases (Nb,ZrO₂, ZrO₂ and Cr₂O₃) formed at the surface. A multilayer AlCrMoNbZr/(AlCrMoNbZr)N coating can be beneficial for preventing Al migration and boehmite phase formation during autoclave corrosion of an AlCrMoNbZr alloy [116]. The multilayer AlCrMoNbZr/(AlCrMoNbZr)N coating with the layer step of 50 nm demonstrated better protective properties compared to 5/5 nm and 10/10 nm multilayers and single-layer AlCrMoNbZr (Figure 6) [117]. Despite the potential application of HEAs as ATF materials for fuel claddings [118–121], their application as protective coatings is challenging due to possible low temperature eutectics, with Zr alloys and complex oxide scales formed after HT oxidation.

Figure 6. Multilayer AlCrMoNbZr/(AlCrMoNbZr)N HEA coatings: (a) cross section TEM image of 10/10 nm coating; (b) mass gains for HEA-coated N36 zirconium alloy after an autoclave test at 360 °C, 18.7 MPa for 30 days; (c) depth distribution of elements in 50/50 nm HEA coating after the autoclave test. Reproduced from [117] with permission by Elsevier.

3.2. Non-Metallic Coatings on Zr-Based Alloys

3.2.1. Nitride Coatings

There are several research groups working on the development of nitride coatings for nuclear fuel Zr claddings. Khatkhata et al. deposited TiN and Ti₃Al₅N coatings on Zry-4 substrates using pulsed laser deposition, and exposed them to supercritical water conditions for 48 h at a temperature of 500 °C and a pressure of 25 MPa [122]. The coated tubes were remarkably intact after exposure, while uncoated tubes demonstrated severe oxidation and breakaway corrosion. The TiN coatings also reduce the hydrogenation of Zr alloys [123]. However, nanocrystalline TiN coatings can dissociate under energetic particle bombardment, forming Ti-enriched zones with low oxidation resistance [124]. Despite good diffusion barrier properties of TiN coatings [125], they are considered less as a protective coating or barrier interlayer because of their large coefficient of thermal expansion (CTE) difference with Zr and possible cracking during thermal cycling [126]. Alat et al. studied the corrosion resistance of TiAlN and TiN coatings deposited on ZIRLO substrates by cathodic arc physical vapor deposition [127,128]. The corrosion tests were implemented in static pure water at 360 °C and 18.7 MPa for 72 h. After the tests, a very low weight gain between 1–5 mg/dm² was observed, whereas the uncoated ZIRLO samples showed an average weight gain of 14.4 mg/dm². However, aluminum depletion in a high-temperature water environment results in the formation of a boehmite phase that de-
grades the corrosion resistance of TiAlN coatings (Figure 7). To eliminate boehmite formation, the deposition of an outer TiN layer or multilayer approach based on TiN/TiAlN coating can be effective [128,129].

Figure 7. Cross-section SEM images of TiAlN/Ti/ZIRLO™ after autoclave testing at 360 °C for 72 h: (a) secondary electron mode, and (b) backscattered electron mode. Reproduced from [127] with permission by Elsevier.

Daub et al. provided comparative analyses on corrosion resistance of 2–4 µm-thick CrN-, TiAlN- and AlCrN-coated Zry-4 alloy [130,131]. It was shown that a CrN coating demonstrates better overall performance in both aqueous and steam environments, as well as twice-reduced hydrogen ingress. Meng et al. showed the high resistance of a 13 µm-thick CrN coating deposited on a Zr-702 alloy in the air up to 1160 °C (Figure 8) [132]. Krejčí et al. demonstrated cracking and local failures of CrN coatings after HT steam oxidation at 1200 °C for 30 min [133]. It was indicated that the cracking was caused by partial decomposition of CrN to Cr₂N at high temperatures (typically below 850 °C) [134].

Figure 8. Weight gain of uncoated and CrN-coated Zr alloys as the function of oxidation temperature in the air (a), and the appearance of the samples after the oxidation tests (b). Reproduced from [132] with permission by Elsevier.

3.2.2. Zirconium Silicide Coatings

Zirconium silicides have high thermal conductivity and favorable mechanical properties [135]. Yeom et al. studied the oxidation behavior of Zr:Si, ZrSi and ZrSi₂ coatings deposited on a Zry-4 alloy by magnetron sputtering [136]. Thicker (3.9 µm) ZrSi₂ coating exhibited oxidation resistance almost two orders of magnitude higher compared to uncoated Zry-4 in 700 °C air for 20 h. The thicknesses of the oxide layers were 7 and 20 µm for coated Zry-4 at 1000 (1 h) and 1200 °C (10 min) steam, respectively. No cracking or
spallation was observed after three cycles of water quenching from 700 °C. However, the brittle nature of silicide coatings and coating volatilization under autoclave testing limit their application for ATF [137].

3.2.3. Carbide Coatings

Silicon carbide is a promising material for ATF Zr claddings since it has a high melting point, low chemical reactivity, superior oxidation resistance at high temperatures and a lower thermal neutron cross-section than Zr-based alloys [138]. SiC coatings deposited on a Zry-4 alloy using co-sputtering of SiC and Si targets demonstrate enhanced oxidation resistance in 900 °C steam due to the formation of a protective silica layer [139]. SiC coatings obtained by magnetron sputtering also reduce the hydrogenation of zirconium alloys under normal operation temperatures [140,141]. The effect of deposition parameters on the mechanical properties of SiC coatings deposited on Zircaloy-4 substrate by magnetron sputtering was shown in [142]. Al-Olayyan et al. showed better adhesion of SiC coating on rough surfaces of Zry-4 alloy, which resulted in higher corrosion resistance [143]. Nevertheless, unstable oxide growth and coating volatilization during autoclave corrosion tests must be considered carefully when designing SiC-based coatings for LWRs [144].

Zr-Al-C coatings obtained on Zry-4 alloy by magnetron sputtering demonstrated poor protective properties during oxidation in steam at temperatures beyond 800 °C due to formation of ZrO2 and Al2O3 oxides scales [145]. Michau et al. studied the protective properties of Cr-based carbide (CrC, CrSiC) coatings deposited on the inner surface of Zr cladding tubes using DLI-MOCVD [146]. Good adhesion and better oxidation resistance of amorphous CrxCy coating in air and steam at 1200 °C were shown (Figure 9), while the addition of Si was ineffective in improving oxidation resistance of chromium carbide coatings. It was also shown that an optimized DLI-MOCVD process can be successfully used to deposit CrCx coatings inside Zr cladding tubes 1 m in length [147,148].

![Figure 9. Mass gains measured by TGA of uncoated and CrxCy-coated Zircaloy-4 under air oxidation isothermal air oxidation at 1200 °C (a); BSE SEM image and oxygen profiles of CrxCy-coated clad segment after oxidation in steam at 1200 °C for 10 min, followed by water quenching (b); and the detailed SEM + EBSD image of the inner surface of CrxCy-coated clad segment after the oxidation test (c). Reproduced from [146] with permission by Elsevier.](image)

Jin et al. deposited 75Cr25NiCr (wt.%) on a Zr-2.5Nb alloy using a high velocity oxygen fuel (HVOF) technique and showed improved oxidation resistance in air and steam at 700–1000 °C [107]. However, the coated samples showed poor corrosion resistance in supercritical water at 400 °C and 10.3 MPa, caused by a bimetallic effect (this coating can build up bimetallic couple with the Zr-2.5Nb alloy, resulting in the acceleration of the corrosion rate). Yang et al. demonstrated high oxidation resistance of 120 μm-thick HVOF CrC2-NiCr coating at 1200 °C in steam for 1 h due to the formation of a dense chromia scale [149]. However, the high coating thickness and heterogeneous/porous microstructure formed by the HVOF method may limit the usefulness of such coatings for ATF Zr claddings.
3.2.4. MAX-Phase Coatings

MAX phases are layered hexagonal carbides and nitrides referenced to the general formula $M_{n+1}AX_n$ (MAX), where “n” ranges between 1 and 4, “M” represents a transition metal (Sc, Ti, V, Cr, etc.), “A” is an A-group (mainly IIIA and IVA, or groups 13 and 14) element and “X” is either C and/or N [150, 151]. MAX phase materials exhibit excellent properties of both metals and ceramics such as high electrical and thermal conductivity, high melting points and excellent oxidation resistance [152, 153].

Alumina-forming MAX phases demonstrate superior oxidation resistance at high temperatures and exhibit self-healing ability [154]. Li et al. investigated high-temperature oxidation resistance of 12 μm-thick Ti$_2$AlC coating on ZIRLO alloy in pure steam at 1000–1200 °C [155]. The coating remains intact and demonstrates good protective properties up to 1200 °C during 5 min oxidation time. The improved oxidation resistance was due to the dense columnar-free microstructure of Ti$_2$AlC coating and triple oxide scale $\alpha$-Al$_2$O$_3$ + rutile-TiO$_2$/ $\alpha$-Al$_2$O$_3$/TiO$_2$. Maier et al. showed the oxidation resistance of cold sprayed Ti$_2$AlC coating (90 μm) in Ar/steam mixture at 1005 °C for 20 min [156]. The Ti$_2$AlC coating protected the Zry-4 alloy from oxidation and had high hardness and wear resistance. Thinner Ti$_2$AlC/TiC coatings (5/0.5 μm) deposited by magnetron sputtering demonstrate high oxidation resistance in steam at 800°C, forming a triple-layered scale ($\theta$-Al$_2$O$_3$/TiO$_2$/ $\theta$-Al$_2$O$_3$) [157]. It was also shown that the TiC barrier layer mitigates the inward diffusion of Al into the Zry-4 alloy. However, rapid oxidation at 1000 °C resulted in cracking and spallation of the Ti$_2$AlC coatings.

The oxidation resistance of Ti-Al-C and Cr-Al-C coatings deposited by magnetron sputtering on ZIRLO alloy was investigated in [158]. Results of the autoclave test at 360 °C and 18.6 MPa showed poor protective properties of Ti-Al-C coatings due to the formation of multiple oxide scale and hydroxide phases. The Cr$_2$AlC coating demonstrates better oxidation performance; however, partial spallation and formation of volatilized AlOOH was also revealed. Tang et al. showed the excellent oxidation resistance and self-healing ability of thin Cr$_2$AlC coatings in steam at 1000 °C (Figure 10) [159].

![Figure 10](image-url)

**Figure 10.** Cross-section images of three types of MAX-phase coatings with barrier layers on Zircaloy-4 after annealing: (a) Ti$_2$AlC, (b) Zr(Al)C, (c) Cr$_2$AlC, and their oxidation kinetics in 1000 °C steam (d). Reproduced from [159] with permission from the authors.

Imtyazuddin et al. analyzed the radiation resistance of magnetron sputtered Cr$_2$AlC films under 320 keV Xe ions at 300 and 623 K [160]. It was found that Cr$_2$AlC films are amorphized at room temperature even at low doses; however, no amorphous phase was found up to 90 dpa at 623 K, indicating good radiation tolerance at elevated temperatures (Figure 11). Furthermore, both Ti$_2$AlC and Cr$_2$AlC coatings reduce hydrogen uptake effectively [161]. Wang et al. also demonstrated good oxidation resistance of 10 μm-thick Cr$_2$AlC coatings in air at 1100 °C [162].
A literature review indicates the rapid diffusion of “A” element from the MAX phases into the Zr alloys with the formation of an interdiffusion layer, thereby decreasing the protective properties of the coating. Thus, various diffusion barrier layers between the coating and the substrate should be considered when developing protective coatings for ATF based on MAX-phases.

4. Mechanism of Protection

Coating methods, materials and deposition parameters play significant roles in oxidation resistance of protective coatings. The key protection mechanism involves the formation of a stable oxide layer on the coating surface with a low oxidation rate. Stable and well-studied oxides include alumina (Al₂O₃), silica (SiO₂) and chromia (Cr₂O₃). Therefore, further discussion will focus mainly on the coatings forming these oxides, especially on chromium-based coatings. One of the important problems considered is the volatilization/sublimation of oxides in water and steam under normal operation and DBA conditions [163]. Among the indicated oxides, chromia is the only stable one that is slowly volatilized/sublimated during autoclave and LOCA conditions [19]. The sublimation rate of alumina and silica is not expected to be a problem at temperatures below 1300 °C; however, noticeable volatilization was shown after autoclave tests in a simulated PWR medium [164]. In addition, the protective coating, as well as the growing oxide layer, should have a dense microstructure to reduce the diffusion of oxygen and hydrogen (generated from oxidation reaction) along the grain boundaries of the coating.
Another serious issue is interdiffusion at the interface of the protective coating and the alloy. Interdiffusion is observed mainly for metallic coatings due to higher diffusion coefficients of species in metals compared to ceramics. Thus, during oxidation of metallic coatings, the coating can be consumed by oxide growth and formation of the interdiffusion layer. Interdiffusion is also aggravated by the fact that eutectic phases with low melting points can form, especially in the case of B-DBA conditions. Therefore, the rates and mechanisms of interdiffusion for each type of coating, as well as methods to inhibit the diffusion, should be revealed and considered in detail.

4.1. Microstructure and Thickness of the Coatings

It is well known that not only the composition of the coatings but also their microstructure and thickness play an important role in their oxidation resistance.

Despite little research, the influence of coating thickness on oxidation resistance has been well studied. Brachet et al. performed comparative analysis of the mass gains for Zry-4 alloy with 1–12 µm-thick PVD Cr coatings after HT steam oxidation at 1100 °C for 850 s [87]. The results demonstrated a reduction of the mass gain of Cr-coated samples from 6.5 mg/cm² to <1 mg/cm², with increasing coating thickness. Kashkarov et al. investigated the oxidation kinetics of Cr-coated E110 alloy in 1200 °C steam for 10 min, depending on coating thickness and microstructure [165]. It was shown that the weight gain of Cr-coated samples was reduced from 22.1 to 4.1 mg/cm², as coating thickness increased from 4.5 to 9.0 µm. A similar observation was shown for a E110 alloy, with magnetron-deposited Cr coatings after HT air oxidation tests at 1100–1200 °C [72].

Protective coatings can provide a significant additional delay before oxidation, as HT becomes too detrimental to the mechanical integrity of the claddings. Accelerated oxidation kinetics of Cr-coated Zr alloys was observed after a transition period, whereby the coating state changed from protective to non-protective (Figure 12a) [166]. The duration of the protective period, as well as transition time, are mainly dependent on coating thickness (Figure 12b).

The mechanism of HT steam oxidation of Cr-coated zirconium alloys was suggested and described in [166]. The oxidation process can be divided into three stages characterized by protective, transition and non-protective behavior (Figure 13). During the protective stage, the oxidation rate is controlled by the growth of the protective Cr₂O₃ outer layer. At the same time, inward diffusion of residual Cr into the alloy results in the formation of a Cr₆Zr interlayer at the interface, while the outward diffusion of Zr occurs along the grain boundaries of the coating. It is also worth noting that oxygen can diffuse along the grain boundaries of the coating to the zirconium alloy, especially in the case of
columnar or porous microstructure of the coatings. The oxidation rate gradually increases during the transition stage, which is probably caused by the formation of a zirconia network at the grain boundaries, enhancing oxygen transport to the alloy. Han et al. and Ma et al. pointed out a reduction-oxidation mechanism between Zr and Cr₂O₃ [95,96], which can lead to partial reduction of Cr₂O₃, thereby slowing down the growth rate of the outer chromia scale. Along with the growth of the outer Cr₂O₃ layer, the continuous oxygen ingress into the Zr alloy leads to the formation of an oxygen-stabilized α-Zr(O) phase beneath the coating, and then the growth of ZrO₂ due to subsequent oxidation of α-Zr(O) and ZrCr₂ phases. During oxidation, the ZrCr₂ interlayer can be transformed into metallic Cr and zirconia grains. At the third stage, the highly oxidized coating demonstrates non-protective behavior and the oxidation rate is mainly controlled by the growth of the zirconia layer.

An analysis of autoclave and high-temperature oxidation tests showed that chromium coatings must be at least 10 µm-thick to provide long-term protection (see Table 2). However, the thickness of protective coatings on Zr-based cladding should be limited to avoid a significant impact on the neutron transport in LWRs. For example, for Cr coatings, thickness should not exceed 30 µm, so that the reduction of fuel cycle life would be limited to 1% [167].

As long as the Cr coating is intact/protective, the microstructure of the Cr coatings is the key characteristic in normal operation and accident conditions [165,168–170]. It has been shown that the activation energy of oxidation is higher for dense Cr coatings compared to columnar ones. It was found that pre-annealing of the Cr coatings on Zircaloy-4 at 700 and 800 °C for 2 h increases the resistance of the coating to oxidation due to an increase in grain size (recrystallization) [166]. The columnar structure of coatings is undesirable, as it significantly decreases their corrosion resistance due to the rapid diffusion of oxygen along the grain boundaries down to the Zr alloy. Thus, it is necessary to maintain an optimal balance in which the coating exhibits high corrosion resistance and acceptable mechanical properties to reduce wear and mechanical damage of coatings during assembly, transportation and operation of fuel element claddings.

To obtain coatings with a dense and uniform microstructure, deposition technology should be optimized to create special conditions for coating growth. For example, during
magnetron sputtering, the ratio of substrate temperature to the melting point of coating material is considered a key criterion [171,172]. To arrive at these conditions, preliminary heating or substrate biasing can be used. Moreover, a perspective approach uses sputtering technologies with a high ion-to-neutral ratio, as present in a magnetron with a closed magnetic field or high power [173,174].

Changes in the composition and crystalline structure of Cr-based coatings affect their corrosion resistance and mechanisms. Ougier et al. studied the air oxidation behavior of Cr-Al-C and annealed Cr:AIC MAX-phase coatings deposited using an HiPIMS technique [175]. It was found that mixed AlO$_3$ and CrO$_3$ phases form at the top surface of the as-deposited Cr-Al-C coating, while a dense and continuous AlO$_3$ layer forms on the Cr:AIC coating at the initial stage of the oxidation test (15–30 min at 1200 °C). However, a porous Cr:C$_3$ interlayer is formed during continuous oxidation due to the outward diffusion of Al and Cr, and the interdiffusion of Cr, Al and C into Zr alloy. Liu et al. showed the effect of Si addition on oxidation resistance of CrAlN coating in steam at 1000 and 1200 °C [176]. A bilayered structure consisting of outer Cr-rich and inner Al-rich mixed Cr and Al oxides layers was formed after oxidation at 1200 °C. It was also found that CrAlN coatings have better oxidation resistance compared to CrAlSiN ones because the latter coatings are easily cracked in HT steam due to the formation of nanosized Si$_3$N$_4$ and SiO$_2$ grains.

**Table 2. Summary of selected protective coatings for Zr-based alloys.**

| Coating/Substrate | Deposition Method | Microstructure | Thickness, μm | Oxidation Conditions | WG, mg/cm$^2$ | Comments | Refs. |
|-------------------|------------------|----------------|--------------|----------------------|--------------|----------|-------|
| Cr/Zry-4          | PVD              | Dense          | 15–20        | PWR medium, 360 °C, 415 °C, 10 MPa, 200 days  
Steam 1200 °C, 1500 s  
3. Steam, 1300 °C, 5600 s  
Air, 1100 °C, 20 min  
Steam, 10 min:  
900 °C          | 0.05             | -Excellent corrosion resistance under autoclave testing;  
-High oxidation resistance in steam under DBA and for short period B-DBA conditions;  
-Enhanced post-quench ductility compared to uncoated alloy;  
-Reduced hydrogen pick-up under HT steam. | [92] |
|                   |                  |                |              | 2.60  
21.20  
2.86 |                  | | |
| Dual MS           | Dense voids-free |                | 4.5          | PWR medium, 900 °C, 1050 °C, 1200 °C  
Steam, 10 min:  
900 °C     | 0.33  
1.40  
22.90 | -Thicker Cr coatings demonstrate higher oxidation resistance;  
-Magnetron sputtering techniques with higher energy per one deposited atom produces better oxidation resistant coating;  
-Coating adhesion affected by substrate oxidation and interface reactions;  
-Transition time into non-protective behavior increases with coating thickness;  
-Interdiffusion of Cr and Zr significantly affects the oxidation kinetics. | [72], [165] |
|                   |                  |                |              | 0.52  
1.60  
12.6 |                  | | |
| Cr/E110           |                  | Columnar       | 6.0          | PWR medium, 900 °C, 1050 °C, 1200 °C  
Steam, 10 min:  
900 °C     | 0.45  
1.00  
4.10 | -Cr-coated alloy corrodes much slower than Zry-4 alloy in both H$_2$BO$_3$-LiOH and dissolved oxygen containing water; | [67] |
|                   |                  |                |              | 0.048  
0.035 |                  | | |
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|----------------------------|
| Coatings                  | Method     | Properties | Notes                                                                 |
| Cr/Zry-4 PVD/HiPIMS       |            | 18.6 MPa, 3000 h Air, 800–1200 °C, 1 h | -Bubbles are observed at the surface of the coated samples after oxidation at 1200 °C. |
|                          | Columnar   | 6.5        | -Cr coatings show better oxidation performance than nitrides (TiN, CrN, TiN/AlTiN, CrN/AlTiN) and metallic alloy (NbV, NbCrTi, Cr/NbCrTi) coatings; |
|                          | Dense/Multi-layered | 3.5 | -Cr-based coatings exhibited good compromise between nominal corrosion resistance and coating adhesion, good fretting wear resistance, as well as improved HT steam oxidation resistance at DBA and slightly D-DBA conditions. |
| NiCr/E110 MS Columnar/Dense | 5–12 | Steam, 1200 °C, 5 min | <1 -Ni-Cr coatings demonstrate low oxidation resistance compared to pure Cr coatings; |
| Ni-Cr/Zry-4 HVOF Dense with closed pores | 120 | Steam, 1200 °C, 1 h | 64.4 -Fast interdiffusion of Ni into the E110 alloy; |
| FeCrAl/Zry-4 (Zirlo) CS Dense | 100 | Air, 1200 °C, 20 min | 0.9 -Formation of a thick interdiffusion layer of (Fe,Cr)Zr Laves phase with low melting point; |
| FeCrAl/Mo/Zrlo dcMS Dense | 6.6/10.6 | Steam, 1000–1200 °C, 1 h | -Mo interlayer can act as a diffusion barrier between FeCrAl and zirconium alloy; |
| Cr/SiC HiPIMS + CAPVD Dense | 5–15 | Steam, 1200 °C, 4 h | 1.2 -HiPIMS and HiPIMS+CAPVD coatings are still intact after steam oxidation, but CAPVD coating is partially delaminated; |
|                          | HiPIMS CAPVD Dense/cracks | 0.9 | -Cr coatings were fully consumed by oxidation and interdiffusion with the SiC and then the rate was slowed down and controlled by SiO2 growth; |
|                          | HiPIMS + CAPVD Dense | 1.5 | -H generation will be significantly lower than in the case of Zr-based alloy claddings. |
| Coating Material | Deposition Method | Microstructure | Weight Loss | Duration | Temperature | Test Conditions | Notes |
|------------------|------------------|----------------|-------------|-----------|-------------|----------------|-------|
| SiC/Zry-4        | PECVD            | –              | 1           | Autoclave, 350 °C, 20 MPa, 24 h | Weight loss | -Unstable oxide growth; -Volatilization and degradation of coating during autoclave test. -Coating volatilization; | [144] |
| ZrSi/Zry-4       | dCmS             | Columnar       | 3.9         | Autoclave, 400 °C, 10.3 MPa, 72 h | Weight loss | -No cracking or spallation are observed after three cycles of water quenching from 700 °C. -Improved HT oxidation resistance of Cr-coated alloy; | [137] |
| Cr/Zry-4         | CAPVD            | Dense          | 10          | Steam, 1200 °C, 2000 s | 12           | -No cracking of the coating after oxidation; -Formation of Cr–Zr interlayer. -Parabolic kinetics at 1130 °C changed to quartic at 1230 and 1310 °C, which is attributed in part to the sublimation of Cr species; | [178] |
| Cr               | CS               | Dense with some closed pores | 50          | Steam, 1130–1310 °C for 10–90 min | –            | -Cr–Zr interdiffusion resulted in the formation of brittle ZrCr; or Zr(Fe, Cr): intermetallics; -Cr-rich precipitates formed in the depth of Zr alloy after oxidation at 1310 °C. -Cr–Al–C and annealed CrAlC coatings protect Zr alloy in dry or wet air; | [179] |
| CrAlC/Zr702      | HiPIMS           | Columnar       | 3.2         | Air, 1200 °C, 2 h | 2–5          | -Mixed Cr2O3 and Al2O3 formed during oxidation; -Outward diffusion of Al and Cr and the interdiffusion at the coating/metal interface led to formation of porous (Cr, C) interlayer. -TiAlC/TiC coating demonstrates high oxidation resistance in steam at 800 °C, forming a triple-layered scale θ-Al2O3 + TiO2/θ-Al2O3/TiO2; | [157] |
| Ti3AlC/TiC/Zry-4 | MS               | Dense voids-free | 5.0/0.5 | Steam, 1000 °C, 250 min | 42.5         | -TiAlC barrier layer mitigates the inward diffusion of Al into the Zry-4 alloy; -Rapid oxidation at 1000 °C resulted in cracking and spallation of the Ti3AlC coatings. | [157] |
| Ti3AlC/TiC/ZrIl0 | hybrid arc/MS    | Dense          | 12.0/1.5    | Steam, 1200 °C, 10 min | 16.65        | -TiAlC coating improves the HT oxidation resistance of ZIRLO alloy during oxidation at up to 1200 °C for 5 min; -Despite TiC barrier layer, the inward diffusion of Al is the main cause of coating failure and rapid consumption for prolonged oxidation times; -Need to prepare thicker coatings and suitable diffusion barriers. | [155] |
| CrAlN/Zry-4      | CAPVD            | Dense          | 5.5         | Ar/steam, 1200 °C, up to 1 h | -17.1 (15 min) | -Bilayer structure of the formed oxides: an outer Cr-rich mixed Cr2O3–Al2O3 layer and an inner Al-rich mixed (Al2O3-Cr2O3 in CrAlN and Al2O3-Cr2O3-SiO2 in CrAlSiN) layer; | [176] |
| CrAlSiN/Zry-4    | CAPVD            | Dense          | 5.8         | Ar/steam, 1200 °C, up to 1 h | -14.8 (15 min) | - |
4.2. Interdiffusion and Eutectics under B-DBA Conditions

The interdiffusion of coating elements has a complex negative effect related to the rapid consumption of the coating and the formation of anisotropic structures inside the Zr alloys, as a result of the formation and subsequent crystallization of liquid eutectic phases. These processes accelerate with increasing temperature, so that the behavior of protective materials under B-DBA conditions is highly important for the development of ATF Zr claddings.

Brachet et al. investigated the behavior of Cr-coated M5 alloy under steam oxidation at 1400–1450 °C for 100 s, followed by water quenching [166]. It was found that the rapid mutual Cr–Zr diffusion during heating is accompanied by the formation of Cr-Zr eutectics at 1305–1325 °C, which are gradually enriched with zirconium along with the growth of the outer ZrO₂/α-Zr(O) oxide layers at the isothermal oxidation period. After water quenching, a dendritic substructure of the Cr-depleted prior-β₂ and Cr-enriched interdendritic zones form inside the alloy, and a "crocodile skin"-like morphology of the coated alloy was observed (Figure 14). Krejci et al. observed similar microstructures of Cr-coated E110 alloy after HT steam oxidation at 1400 °C for 2 min [134]. A higher Cr content was found in the region of the prior β₂ phase (with lower oxygen content).

Interdiffusion also shows a negative effect on FeCrAl-coated Zr alloys [180]. In this case, the fast diffusion of Fe and Cr resulted in the formation of brittle intermetallic compounds such as Fe₂Zr, Fe₃Zr, Fe₅Zr and Zr(Cr,Fe)₂, as well as in a low melting-point of Zr-Fe or Zr-Fe-Cr eutectic phases [81,85,181]. Thus, the eutectic phases and the mismatch of CTE between Zr alloy and intermetallics can cause the formation of a non-protective scale on the oxides and the generation of micro-cracks. Wang et al. demonstrated the oxidation behavior of FeCrAl coating, with a ZrO₂ barrier layer formed by plasma electrolytic oxidation (PEO) on a Zr-4 alloy surface. It was found that a 10–15 μm-thick ZrO₂ layer eliminates the diffusion of Fe and Cr to the alloy in steam at 1000 °C [182]. Nevertheless, more detailed studies of oxidation behavior at higher temperatures are needed. Han et al. demonstrated good barrier properties of a 10.6 μm Mo interlayer between a 6.6 μm FeCrAl coating and a Zr-4 alloy under steam oxidation up to 1200 °C [177]. Despite the better oxidation resistance of FeCrAl/Mo coatings, a strong interdiffusion between Mo and FeCrAl layers at 1200 °C resulted in the formation of a FeCrMo interlayer, accompanied by generation of Kirkendall voids in the FeCrAl coating.
Krejci et al. investigated a stoichiometric CrN interlayer deposited by magnetron sputtering as the barrier against Cr-Zr interdiffusion at HT steam oxidation [183]. It was found that a thin ZrN layer formed beneath the coating due to the inward diffusion of nitrogen generated from the decomposition of CrN to Cr$_2$N phase. The 13 μm-thick CrN layer inhibited the diffusion of Cr to Zr alloy, and demonstrated high oxidation resistance at temperatures above the Cr-Zr eutectic (1350 °C) for only a short period (Figure 15). Tang et al. showed that a 500 nm TiC interlayer mitigates the rapid diffusion of Al from Ti$_2$AlC coating into the Zry-4 alloy, which resulted in a prolonged oxidation resistance of Ti$_2$AlC/TiC coating under 800 °C steam [157]. However, both Ti$_2$AlC and Ti$_2$AlC/TiC coatings demonstrated low oxidation performance at temperatures higher than 1000 °C.

The abovementioned studies confirm the promising approach of barrier layers for suppressing interdiffusion between protective coating and zirconium alloys under B-DBA conditions. However, there are many factors that should be considered when choosing an intermediate layer, such as possible formation of eutectic phases, low melting point, high diffusion coefficient in Zr, large difference in thermal expansion coefficients, possible phase transitions, etc. Table 3 shows some of the possible interlayers between Cr coating and Zr alloys, and indicates their most important properties in terms of barrier coating for ATF. Diffusion coefficients in zirconium strongly depend on the presence of impurities, and their reported values differ significantly in the published works. Therefore, only relative diffusion characteristics (coefficients) are given in Table 3 for comparison. Considering interlayer materials, their thermal neutron cross-sections should also be discussed.
in view of possible changes in neutron economy [184]. The multiplication factor, reactivity, neutron spectra and reactivity coefficient will change even with very thin coatings [185]. It can limit interlayer thickness to minimize neutron losses.

Figure 15. Microstructure of Cr/CrN-coated Zr-1%Nb alloy after HT oxidation in steam at 1365 °C for 2 min: SEM image and corresponding EDS line scan. Reproduced from [183] with permission by Elsevier.

Table 3. Comparison of properties of possible barrier layers between Cr-based coatings and zirconium alloys. Zirconium and chromium are presented for comparison.

| Interlayer | Possible Eutectics | Tm, °C | Diffusion Coefficient in β-Zr | Solubility in β-Zr at 1300 °C | CTE at RT, 10^-6 K^-1 | λ, W/m/K | Phase Transitions | Mechanical Behavior |
|------------|--------------------|--------|------------------------------|--------------------------------|------------------------|---------|------------------|-------------------|
| Zr         |                    | 1855   | -                            | -                              | 7.2 (hcp)              | 9.6 (bcc) | αhcp → βbcc at 862 °C | Ductile           |
| Cr         |                    | 1907   | High                         | <8 at.%                        | 6.5                    | 93.7     | no               | Ductile/Brittle   |
| Mo         |                    | 2623   | Low                          | <30 at.%                       | 5.5                    | 138      | no               | Ductile           |
| Ta         |                    | 3017   | Low                          | ~15 at.%                       | 6.5                    | 57.5     | Only metastable β → α at 750-775 °C | Ductile           |
| Nb         |                    | 2477   | High                         | 100 at.%                       | 7.1                    | 53.7     | no               | Ductile           |
| Re         |                    | 3186   | Unknown                      | ~10 at.%                       | 6.1-6.6                | 39.6     | no               | Ductile           |
| CrN (Cr2N) |                    | 1770   | N diffusion due to CrN → Cr2N | -                              | 9.0-9.4                | 2.5 (CrN); 12 (Cr2N) | CrN → Cr2N at HT | Brittle           |
| Cr2O3      |                    | 2330   | -                            | -                              | 7.1                    | 12       | no               | Brittle           |
| ZrO2       |                    | 2715   | -                            | -                              | 7 (m-ZrO2); 12 (t-ZrO2) | 1.7 (m-ZrO2) | t → m-ZrO2 (high volume expansion) | Brittle           |
| ZrC        |                    | 3532   | -                            | -                              | 6.7                    | 20.5     | no               | Brittle           |
| 3C-SiC     |                    | 2830   | -                            | -                              | 4.3                    | 270      | no               | Brittle           |

Note: Tm—melting point, CTE—coefficient of thermal expansion, RT—room temperature, λ—thermal conductivity.

Molybdenum is considered one of the most promising interlayers since it shows good barrier properties, a CTE similar to Cr, high thermal conductivity, a high melting point and an acceptable neutron cross-section (2.5 barn). Moreover, the potential eutectic phase of Mo-Zr has a higher melting temperature (1550 °C) compared to Cr-Zr (1330 °C). Nevertheless, coupled effects of the Cr-Mo-Zr system (eutectics) should be considered. Recently presented results obtained at CEA showed some interesting and positive observations on Cr/Mo-coated zirconium alloy (not published yet, but please see Michau et al.,
It has been shown that a Mo/Cr coating demonstrates good oxidation resistance in steam up to 1400 °C for 100 s. The Mo interlayer can delay the Cr-Zr eutectic reaction and reduce Cr consumption by interface reactions. However, detailed studies on coating architecture, adhesion, irradiation behavior and oxidation resistance under normal operation conditions are still required.

A tantalum interlayer can also be promising for enhancing the performance of Cr-coated alloys under B-DBA conditions, since it has a low diffusion coefficient and solubility limit in β-Zr phase, as well as CTE close to Cr. In addition, melting temperatures of possible eutectic phases are higher than that of the Cr-Mo-Zr system. The thermal conductivity of Ta is lower than that of chromium, but higher than that of zirconium. However, the high thermal neutron cross-section of Ta (20.6 barn) can strongly limit the thickness of the Ta layer in the protective coating, thus saving of neutron economy and decrease neutron losses. Unfortunately, there are no studies on Ta diffusion in zirconium at high temperatures and HT oxidation of Cr/Ta/Zr or Ta/Zr systems. Despite a lack of studies, a Ta interlayer could potentially be effective and should be studied in future research.

Niobium is already used as an alloying element in Zr-Nb alloys and has a high melting point in the Nb-Cr and Nb-Zr systems, and a CTE close to that of zirconium. Nb has a low diffusion coefficient in α-Zr phase [181] and a neutron cross-section of 1.2 barn. However, high interdiffusion between Nb and Zr is expected due to the unlimited solubility of Nb in the β-Zr phase at temperatures above 970 °C, which is also supported by high values of diffusion coefficients measured between Nb and Zr in the β phase, including Nb in Zr1Nb alloy [186,187].

Rhenium is a transition metal with a very high melting point (3186 °C), which forms a eutectic phase with Zr at high temperature (1600 °C) and has a low solubility limit in the β-Zr phase. The CTE of Re is close to that of Cr, while thermal conductivity is between Cr and Zr. However, Re is one of the rarest elements and has a very high neutron cross-section (89.7 barn); therefore, this material is considered economically unfavorable in terms of supply risk, environmental implications and vulnerability to supply restrictions [188].

Ceramic coatings such as CrN, Cr2N, ZrO2, ZrC and SiC are also good candidates for barrier interlayers due to their high temperature stability, high melting point and low diffusion rate compared to metallic coatings. CrN coatings demonstrate barrier properties at temperatures above 1350 °C; however, only for thick interlayers, as described above. The decomposition of CrN → Cr2N results in the formation of a zirconium nitride layer, which also plays an important role in reducing the diffusion of Cr into Zr alloy. The CTE of CrN is similar to that of the β-Zr phase. Nevertheless, a very low thermal conductivity of chromium nitrides coatings and the phase transformation (fcc to hcp) accompanied by volume reduction should be taken into account when selecting thick CrN layers as interlayer coatings. Zirconium carbide can be potentially used since it has an intermediate CTE and thermal conductivity comparable to that of Zr. Silicon carbide, and with a cubic (3C) structure that is well-studied since it is one of the most prospective materials for ATF claddings [189–191]. However, its significantly lower CTE compared to Cr and Zr, as well as possible reactions with Zr, limit its application as a barrier interlayer coating for B-DBA conditions. The literature data showed good barrier properties of ZrO2; for example, in the case of FeCrAl coatings [182]. When choosing such a type of interlayer, it is necessary to take into account its very low thermal conductivity and possible phase transformation (t-ZrO2 → m-ZrO2) with high volume expansion. Therefore, detailed studies of the barrier properties of ZrO2 and its behavior under high-temperature oxidation conditions are required. In addition to the other coatings, Cr2O3 can also be a promising material for a barrier interlayer, as it has a suitable CTE and good oxidation resistance.

Although the barrier properties of ceramic coatings are more advantageous, they are brittle, and small changes in CTE with temperature can lead to the formation of microcracks and coating failures at the coating/alloy interface. Multilayer ceramic coatings can be more resistant to coating interruption if they are composed of alternating brittle
and elastic layers. Musil demonstrated [192,193] two approaches to prevent cracking of brittle coatings. The first way comprises the deposition of a highly elastic over-layer on top of the brittle layer, while the second is the reduction in the macrostress of multilayered structures [194]. Therefore, a multilayer approach with an appropriate design can be an effective way to reduce the CTE difference and improve the cracking resistance of protective ceramic coatings. Moreover, multilayers can be used as a barrier layer to prevent Cr–Zr interdiffusion, while a top chromium coating with high thickness can act as the main protective layer.

Sidelev et al. demonstrated the barrier properties of multilayer CrN/Cr (250/250 nm) coatings against Cr–Zr inter-diffusion during heating up to 1400 °C (Figure 16) [195]. It was found that the diffusion limitation was attributed not only to CrN layers but also to a ZrN layer formed beneath the multilayers due to the decomposition of chromium nitrides at high temperatures (650–900 °C). Furthermore, a better oxidation performance of CrN/Cr coatings compared to metallic Cr coating was shown during air oxidation at 1100 °C for 10–40 min. No coating cracking or local oxidation were observed for multilayer coatings with layer steps of 250/250 and 500/500 nm, while multilayer 50/50 nm coating demonstrated accelerated oxidation after a 30 min test.

**Figure 16.** In situ XRD patterns of an E110 alloy with single-layer Cr (a) and multilayer Cr/CrN (b) (layer step-250 nm) coatings under linear heating in the temperature range of 25–1400 °C. Replotted from [195].

### 5. Concluding Remarks

In summary, various coatings for ATF zirconium alloy claddings are considered. The protective properties of coatings under conditions simulating normal and accidental operation of LWRs have been analyzed. Positive and negative aspects of metallic and non-metallic coatings for ATF applications were considered. Several ceramic coatings, e.g., chromium nitrides and carbides, show good results in high-temperature oxidation, but their brittle nature and difference of thermal expansion coefficients with Zr alloys largely limit their use as a single-layer protective coating on outer Zr cladding surfaces. Promising radiation-resistant coatings based on MAX-phases have good protective properties up to 1000 °C; however, they show poor oxidation resistance at higher temperatures or should have high thickness. High-entropy alloys are promising as cladding materials, but display poor corrosion resistance in pressurized water due to the formation of complex heterophase composition of the oxides, some of which may dissolve in water under normal operation conditions. Chromium oxide (Cr$_2$O$_3$) is the most stable oxide phase in water and steam, which is why a dense protective chromia scale is the most preferable option for ATF applications.

Our analysis of the literature data indicates promising uses for Cr-based coatings for normal, DBA and B-DBA conditions. The application of various industrial deposition technologies to deposit Cr coatings onto Zr-based alloys has been shown. Physical vapor
deposition, primarily multi-cathode magnetron sputtering or HiPIMS have great prospects for the development of coating technology for ATF Zr-based claddings. The optimization of deposition parameters to obtain dense columnar-free Cr coatings with high adhesion and mechanical characteristics has been carried out. The technology of magnetron sputtering on full-length Zr-based fuel claddings was developed by CEA. In addition, fuel Zr claddings with Cr-based coatings are currently undergoing in-pile testing; for example, in the Russian research reactor MIR. Nevertheless, an important and relevant issue remains related to the behavior of protective coatings under B-DBA conditions, where strong mutual diffusion between the coating and the zirconium cladding can be expected. This effect is evident in most metallic coatings (including chromium), as well as MAX-phase coatings, even at temperatures below DBA. Accordingly, an important future step is the development of barrier layers that can limit interdiffusion and also meet the basic requirements for reactor materials. This review showed the results achieved for protective coatings with barrier layers, and suggested possible interlayers and designs of multilayer structures that might be considered in the future. Therefore, the selection of appropriate diffusion barrier layers, such as Mo, Ta, ZrO₂, Cr₂O₃, ZrC, etc., is still open for investigation. The thickness of the barrier layer and the protective coating should be determined in view of neutron economy, oxidation resistance and barrier efficiency. For the most promising systems, out-of-pile and in-pile testing of protective coatings with barrier layers are necessary. In the case of ceramic barrier layers, cracking resistance must be clearly studied.

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Abbreviations: Accident Tolerant Fuel (ATF), Beyond Design Basis Accident (B-DBA), Boiling Water Reactor (BWR), Cathodic Arc Physical Vapor Deposition (CAPVD), Coefficient of Thermal Expansion (CTE), Cold Spraying (CS), Design Basis Accident (DBA), Direct Liquid Injection – Metalorganic Chemical Vapor Deposition (DLI-MOCVD), Equivalent Cladding Reacted (ECR), High Entropy Alloy (HEA), High Power Impulse Magnetron Sputtering (HiPIMS), High Temperature (HT), High Velocity Oxygen Fuel (HVOF), Light-Water Reactor (LWR), Loss of Coolant Accident (LOCA), Magnetron Sputtering (MS), Plasma Enhanced Chemical Vapor Deposition (PE-CVD), Pressurized Water Reactor (PWR), Physical Vapor Deposition (PVD), Reaktor Bolshoy Moschnosti Kanalniy (RBMK), Research and Development (R&D), Silicon Carbide (SiC), Water-Water Energetic Reactor (VVER), Weight Gain (WG), Zirconium Low Oxidation (ZIRLO).
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