Zirconium-Based Cladding Coating Technique for Oxidation, Corrosion and Embrittlement Reduction at High-Temperature: An Overview

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Abstract. Fukushima Daichii accident attracted attention to one important factor for nuclear reactors safety – overcoming the high hydrogen emissions under accident conditions. The coating on zirconium-based cladding is one of significant approach to protecting the cladding materials from corrosion, accelerated oxidation at high temperature, embrittlement and (oxygen and hydrogen) uptake at aggressive water-chemical environments inside the core of Light Water Reactors (LWR). This paper presents a compact review of the most common technologies used to apply coating on zr-based cladding superstrates. The paper also discusses the coating materials, substrate preparations and recent advances in deposition techniques.

1. Introduction
Zirconium alloys are extensively used in Light water reactors (LWRs) structural components as fuel claddings due to good physical and mechanical properties which show good performance during normal operation [1, 2]. Many new zirconium alloys cladding materials have been developed by optimizing (Zr-Nb) and (Zr-Sn) alloys series to obtained new zirconium alloys, such as ZIRLO, X5A, and E635 which have corrosion resistance better than Zircaloy-4 [3]. However, the interaction of Zirconium cladding with steam becomes more significant at a temperature greater than 1200 °C which lead to the rapid oxidation of cladding materials [4]. Increasing the production of hydrogen due to zirconium oxidation by high-temperature steam is one of the areas currently being study to make fuel systems inherently safer in the accidents situations, especially after what happened in Fukushima Daichii Reactor [5]. The coating on existing Zr-based claddings is one approach proposed to overcome the rapid oxidation of zirconium alloys at high-temperature and enhance of its corrosion/oxidation resistance during normal operations and accidents condition [6, 7]. In the selection of the coating materials, one must consider a number of important physical and chemical properties such as corrosion resistance, thermal conductivity, thermal stability, adhesion property, high melting point, hydrogen absorption, strength and creep resistance [8]. There are many coating techniques that have been widely investigated for cladding coatings such as thermal spray, physical vapor deposition PVD and chemical vapor deposition CVD [9].

In this review, a brief outline of the previous and current research on the coating materials and their methodology applied to zr-based cladding to protect it against the accelerated oxidation at high-temperature steam is presented.
2. Coating Techniques

Coating technologies are widely used in the industry to enhance the mechanical properties of materials such as resistance to corrosion and wear without a change in the base material. Consequently, this technology was considered by researchers for zirconium alloys cladding materials to slow down oxidation at elevated temperature [10]. One of the most widely used coating/deposition methods is the Chemical Vapor Deposition CVD [11]. Chemical deposition method was used to make a nickel coating on E125 zirconium alloy (Zr-2.5% Nb) which showed the highest efficiency at temperatures up to 800°C [12]. Other commonly used methods for applying coating on the substrate surface layer include Physical Thermal Deposition (PVD) at several variations, evaporative deposition, cathodic arc deposition for instance, pulsed laser deposition, electron beam PVD and sputter deposition. The schematic diagrams in figure 1 show some different coating methods [13].

![Figure 1. a) Vacuum evaporation system. b) Sputtering deposition system. c) Pulsed laser deposition PLD system[13].](image)

The schematic diagram shown in figure 2 describes the Plasma Immersion Ion Implantation (PIII) method used in implanting Titanium into Zr–2.5Nb alloy which improved the mechanical properties of zirconium substrate [14].

![Figure 2. Schematic diagram of the PIII technique [14].](image)

As shown in figure 3, schematic drawings of two different methods of plasma spray (PS) and Laser beam scanning (LBS) used to apply a Si-coated layer on the Zircaloy-4 sample [10].
Figure 3. a) plasma spray method (PS) method. b) Laser beam scanning (LBS) method [10].

Thermal spray coating method which melted or heated particles (1–50 µm) and accelerated to high velocities [15]. The High-Velocity Oxygen Fuel (HVOF) spraying method used to protection of (Zr-2.5Nb) zirconium alloy by Cr$_3$C$_2$–NiCr coating [16]. Cold spray (CS) process also used for coatings on optimized ZIRLO™ [17].

2.1. Coating Materials on Zr-based cladding

The selection criteria of coating materials on Zr-based cladding as same as that taken into account when selection the elements for alloying of zirconium [8]. Table 1, shows some coating elements properties.

| Element | Thermal neutron absorption cross-section (Barns) | Melting temperature (°C) | Thermal Conductivity (W/(m·K)) | Oxide | Oxide Melting temperature (°C) |
|---------|-----------------------------------------------|-------------------------|-------------------------------|-------|-------------------------------|
| Zr      | 0.18                                          | 1855                    | 22.6                          | ZrO$_2$ | 2715                          |
| Ti      | 6.4                                           | 1668                    | 22                            | TiO$_2$ | 1843                          |
| Cr      | 2.9                                           | 1850                    | 94                            | Cr$_2$O$_3$ | 2435                        |
| Fe      | 2.4                                           | 1539                    | 80                            | Fe$_2$O$_3$ | 1565                        |
| Ta      | 21                                            | 3017                    | 57                            | Ta$_2$O$_5$ | 1872                        |
| Nb      | 1.2                                           | 2477                    | 53.7                          | NbO$_2$ | 1915                          |
| V       | 4.8                                           | 1910                    | 30.7                          | VO$_2$  | 1967                          |
| Al      | 0.22                                          | 660                     | 237                           | Al$_2$O$_3$ | 2044                        |

Many pure elements coating were used to protect the surface of Zr-based cladding, Ti (Titanium) element have good physical properties such as high melting point, thermal conductivity and neutron absorption cross-section which lead to its use as a coating material on z-alloys [18]. Metallic chromium (Cr) has good resistance to high-temperature oxidation which results in it being used as a coating material on Zr-alloys by different coating technologies [19]. Cold spray method is used to apply Cr-coated on Zircaloy-4 material [20]. Also Cr-coating have been deposited on Zircaloy-4 by Arc Ion Plating technology to protect it from high-temperature steam oxidation [21]. AREVA enhanced ATF developments by Cr-coated on M5 cladding [22]. FeCrAl alloys, have good corrosion resistance and high-temperature steam oxidation resistance [23, 24], which protect Zr metal slugs up to 1300 °C when used as coating with Type 310 austenitic stainless steel [25]. FeCrAl coatings deposited on Zircaloy-2
by magnetron sputtering, the samples tested in 700 °C steam, no coating degradation was observed [26]. Nitride ceramic coatings (TiN) also shows good result in corrosion/oxidation resistance when used as a coating on Zr-based claddings [27]. TiN films deposition with Ti-implanted Zr-1Nb alloy by filtered cathodic vacuum arc deposition (FVAD) magnetron sputtering, has been shown to protect (Zr-1Nb) alloy from hydrogen embrittlement [28]. Multilayer (TiN, TiAlN) coatings were deposited onto ZIRLO® cladding by cathodic arc PVD, the corrosion tested in static pure water at (360 oC, 18.7 MPa) for up to 90 days, the results observed best corrosion performance was provided and weight gains six times lower compared by uncoated ZIRLO® [29]. Multilayer Cr-Zr/Cr/Cr-N coatings deposited by the vacuum-arc evaporation technique to protect zirconium alloys from high-temperature oxidation in the air [30]. Some types of carbides, (SiC and SiC/SC) and their composites were investigated to be used as a cladding material in light water reactors[31, 32]. SiC was deposited on Zircaloy-4 substrates Chemical vapor deposition (CVD) high adhesion strength and corrosion resistance were obtained [30]. Polycrystalline diamond coated applied on Zircaloy-2 fuel tubes used microwave plasma enhanced chemical vapor deposition apparatus with linear antenna delivery, and the test showed that the diamond layer protect the zirconium against hot steam oxidation[33]. The surface of zirconium alloy (ZIRLO) was also protected by Nanocrystalline diamond layer against oxygen and hydrogen uptake [34].

3. Conclusion

- Different types of coating materials such as single, multilayer, metallic and ceramic materials have been used, and they showed good results for protecting the zr-based cladding from high oxidation, corrosion Oxygen/hydrogen uptake.
- The coatings on zr-based cladding were developed to protect the base materials from water side corrosion and rapid oxidation at high temperature, so it is important the coating layers should be highly stable and well adherent/coherent with the base material.
- One of the major challenges to the structural integrity of coating layers is strain mismatch between coated layer and zircaloy during increasing burnup, due to their different irradiation induced axial growth and creep deformation [35].

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