



# Protective layers of zirconium alloys used for claddings to improve the corrosion resistance

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**Abstract.** Zirconium alloys are used as a cladding material for fuel elements in nuclear reactors. In the case of severe accident conditions, the possible rapid oxidation of zirconium in steam or/and air may result in intense hydrogen generation and hydrogen–oxide mixture explosion. Advanced technologies for increasing the corrosion resistance of claddings are being investigated in two directions: (a) protective coatings on Zr alloys and (b) the use of new materials for claddings. Coatings with silicon may provide a more protective barrier than the  $ZrO_2$  films formed on an alloy cladding during nuclear plant operations. These coatings may also serve as a protective barrier during high-temperature accidents. The current work aimed at developing protective coatings with silicon on zirconium alloys. Multielemental Zr–Si–Cr coatings were formed on Zry-2 alloy using the physical vapor deposition (PVD) method. Long-term oxidation tests were carried out under the following conditions: 360°C/195 bar/63 days/water-simulating PWR water. Obtained results show the protective character of formed layers. The material in the form of silicon carbide grains covered with yttrium–aluminum garnet (SiC + YAG) was prepared using the sol–gel method. The formed powder is the main component for coating formation on Zr–1Nb alloy using the method of suspension plasma spraying (SPS).

**Keywords:** Claddings • Nuclear reactors • Oxidation • Protective coatings • Zirconium alloys

## Introduction

Zirconium alloys, due to their good water-corrosion and radiation resistance at normal working conditions of nuclear reactors, are used as cladding material for fuel elements. Under loss of coolant accident (LOCA) conditions, the possible extremely rapid oxidation of zirconium in a steam atmosphere or air/steam mixture at temperatures  $>800^\circ\text{C}$  results in intense hydrogen generation and possible hydrogen–oxide mixture explosion. From the nuclear reactor safety point-of-view, improvements are required in the areas of nuclear fuel composition, cladding integrity, and the fuel–cladding interactions. Improvement of the oxidation resistance of zirconium alloys at normal operating conditions ( $300^\circ\text{C}$ ) has been investigated over the past few decades [1]. Materials with better tolerance to high-temperature oxidation have been proposed in connection with concepts of accident tolerant fuels (ATFs) and accident tolerant materials (ATMs) [2, 3]. Advanced cladding technologies for increasing the claddings' corrosion resistance are being investigated in two ways: (i) developing new materials and (ii) protective coatings on Zr alloys. In the case of new materials research, some of the issues ought to be resolved: the effect of

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different thermal neutron absorption cross-sections, the impact of radiation hardening and embrittlement on cladding, pellet-cladding mechanical interaction behavior, and oxidation behavior in steam at high temperature [4]. Examples of such materials are stainless steel, FeCrAl alloys, and refractory alloys based on Mo, Nb, Ta, W, and SiC/SiC matrix ceramic composites. Highly adherent oxidation-resistant coatings can be an alternative to bulk materials for cladding. Issues to be resolved here include: coating can be easily regenerated, matching the coefficient of thermal expansion is important, and withstanding the diametrical compression that results from reactor pressurization. Examples of such materials are coatings with silicon [5], chromium, aluminum, and FeCrAl [6, 7], MAX phases [8], and ceramics and carbides –  $Y_2O_3$ ,  $SiO_2$ ,  $Cr_2O_3$ ,  $Cr_3C_2$ , SiC, and ZrC [9].

The coatings with silicon have good resistance under high-temperature conditions. Particularly, they may provide a highly protective barrier than the native  $ZrO_2$  films formed on cladding during nuclear plant operations and a protective barrier during high-temperature accident scenarios [2, 3, 8, 9]. The phase diagram for zirconium–silicon systems shows the existence of intermetallic compounds with different stability regions. For example,  $ZrSi_2$  is stable up to 1620°C,  $ZrSi$  is stable up to 2210°C, etc.

Silicon carbide (SiC) is the most corrosion-resistant ceramic used in mechanical seals and pump parts. It maintains its strength up to 1400°C. It has high-corrosion and heat-resistance properties and excellent thermal conductivity. The SiC coating is dense and wear-resistant. The limitation of SiC applications is associated with its possible decomposition into gaseous phases at about 2500°C. Adding metallic elements or ceramics such as Al, Cu,  $ZrB_2$ , or  $ZrO_5$  can prevent the oxidation of SiC. The incorporation of protective ceramics such as yttrium aluminum garnet (YAG) was tested [3, 10]. Thermal barrier coating (TBC) systems were developed to protect critical components even under demanding operating conditions, especially heat and corrosion. TBCs can be produced using different techniques [11], and the suspension plasma spraying (SPS) method was proposed to form a protective layer on zirconium alloy [12].

The aim of the present work was to develop protective coatings with silicon on zirconium alloys. The Institute of Nuclear Chemistry and Technology (INCT) proposals of protective coating formation on zirconium alloys were/are: (i) multielemental (Zr–Cr–Si) coatings and (ii) (SiC + YAG) coatings.

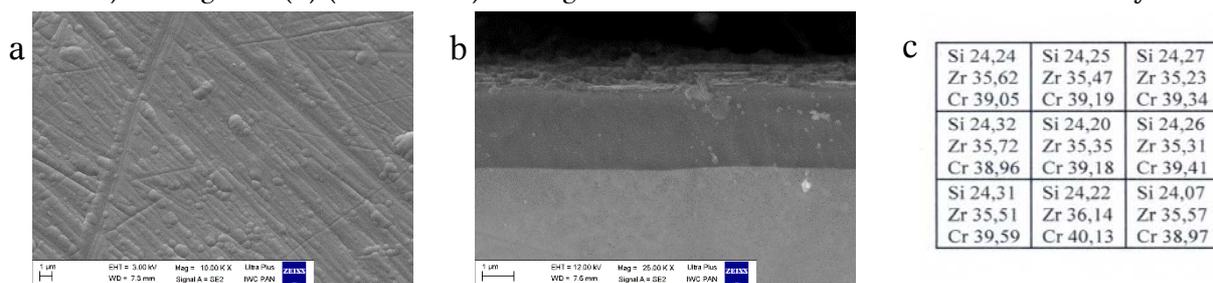
Materials were investigated and characterized by surface-morphology observations using the scanning electron microscope HR SEM ULTRA (Zeiss), by elemental composition determination performed using the EDS system Quantax 400 (Bruker), by phase analysis performed using the X-ray diffraction (XRD) Bragg–Brentano geometry with  $Cu K\alpha$  – Advanced 8 (Bruker), by mass changes measurements performed using the balance Mettler Toledo EXCELENCE XS 105, by oxidation-resistance determination using the oxidation test under standard conditions for pressurized water reactors (PWRs) with an autoclave at Parr 4653, 360°C/195 bar/63 days.

### INCT proposal: multielemental (Zr–Cr–Si) coatings

Zirconium alloy Zircalloy-2 (Zry-2) (Westinghouse) with the elemental composition (wt%): Sn 1.3–1.6, Fe 0.07–0.20, Cr 0.05–0.16, Ni 0.03–0.08, and Zr-balance was used. The coatings formation processes were carried out using the physical vapor deposition (PVD) method at the Łukasiewicz Research Network – The Institute for Sustainable Technologies (Radom, Poland) using the Balzers system facility. Two magnetron targets, metallic Cr and ceramic  $ZrSi_2$ , were used. A clearly oriented surface morphology was the result of initial material surface morphology. The obtained PVD layer was so thin that the surface morphology of the initial material was mapped. Agglomerates, grains, and cracks of the deposited material were visible at the surfaces (Fig. 1a). The presence of elements in the modified surface layer was determined as (wt%): Si, 24.2; Cr, 36.0; and Zr, 39.8. Zry-2 samples with a thickness of 2.5  $\mu m$  were obtained (Fig. 1b). The homogeneity of the  $Zr_{40}Si_{24}Cr_{36}$  coatings was proved by the EDS point analysis method applied to the nine areas of the area visible on the image with 1000 $\times$  magnification (Fig. 1c).

The long-term oxidation test was carried out in the Institute of Nuclear Chemistry and Technology (INCT) in Warsaw, Poland, using process parameters such as 360°C/195 bar/water simulating water used in PWR/63 days. Water used in the autoclave experiments was simulated water from PWR reactors: [Li] = 2–2.2 ppm and [B] = 600–1000 ppm. The surface of the samples became rough with irregular structures and visible morphological objects like grains and agglomerates (Figs. 2a and 2b).

The oxide layer was formed at the sample surfaces of the initial material and coated with  $Zr_{40}Si_{24}Cr_{36}$  materials. The thickness of these layers after



**Fig. 1.** Physical vapor deposition  $ZrSi_2 + Cr$  modified Zry-2 surface (a) SEM image X 10 000, (b) cross-section, (c) homogeneity of the Zr–Si–Cr coatings (wt%) at nine areas of the modified Zry-2.

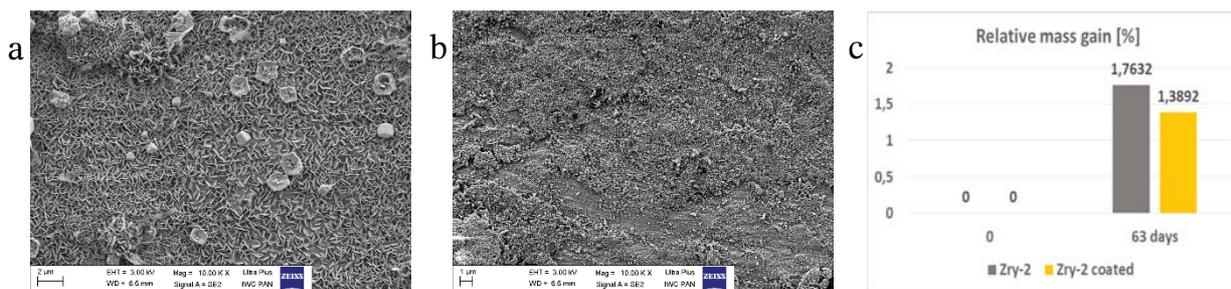


Fig. 2. SEM images with X 10 000× magnification of the material surfaces after 63 days oxidation test (a) Zry-2 and (b) Zry-2 coated with Zr40Si24Cr36, (c) mass changes of Zry-2 and Zry-2 coated with Zr40Si24Cr36.

63 days of test were: (i) for Zry-2: 2.016 μm and (ii) for Zry-2 coated with Zr40Si24Cr36: 0.914 μm. In the case of coated samples, the formed oxide layer was thinner by 45% as compared with the uncoated one. Results of the mass-change measurements show the difference in relative mass gain (Fig. 2c). The relative gain in weight after 63 days of the test was (in%): (i) for Zry-2: 1.7632 and (ii) for Zry-2 coated with Zr40Si24Cr36: 1.3892 as compared with the pre-tested samples. In the case of coated samples, the weight gain was <0.4% in the uncoated sample.

The oxidation process of the Zr40Si24Cr36 coatings occurred, and the base material remained not oxidized. The deposited Zr40Si24Cr36 layer protected the Zry-2 from oxygen migration and slowed down Zry-2 alloy oxidation. The protective mechanism is assumed based on two facts: Cr diffusion to the surface of the coating and presence of high-temperature stable (Si, Zr) compounds [13].

INCT proposal: (SiC + YAG) coatings

The commercial silicon carbide with 400 mesh particle size ≥97.5% (Aldrich Chemistry, USA) was used for the investigations.

In the first step, YAG in the form of Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> was obtained using the INCT procedure with sol Al–Y (pH = 3.5) [14]. Y–Al sol and SiC powder were mixed. Then, the processes of gelation 90°C/6 h/air and calcination 1200°C/3 h/argon were carried out. Detailed morphological investigations show the presence of a thin layer at the surface of the SiC (Fig. 3a). The thickness of the surface layer was estimated to be 60 nm (Fig. 3b). Elemental analysis confirmed the presence of main elements: Si and C from SiC and Y, Al, and O from YAG (Fig. 3c). YAG with a composition of Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> was obtained on the SiC grains.

Crystallographic phases were identified by the XRD method in Bragg–Brentano geometry. The SiC structure was identified in the spectra. This fact was confirmed by the presence of peaks in the positions corresponding with the theoretical SiC spectra: 2θ = 35.5°, 41°, and 59.5°. The Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> structure was identified in the spectra. This fact was confirmed by the presence of strong peaks in the positions corresponding with the theoretical Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> spectra: 2θ = 27.5°, 33°, and 41°. The analyzed spectra confirmed the presence of SiC and formed YAG–Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>.

In the second step, the SPS process is prepared for and will be performed at the Department of Metal Forming, Welding and Metrology, Faculty of Mechanical Engineering, Wrocław University of Technology, Poland. The material obtained in the first step implies that the SiC grains coated with YAG–Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> is the main component used in the plasma-spraying process. Two aspects of the protective character of YAG were considered: (i) in the case of powder used in the plasma-spraying process, a protective mechanism is assumed so as to protect the SiC against decomposition at high temperatures and (ii) in the case of coating: SiC coatings will play a protective role for zirconium alloys.

Conclusions

Improvement of the oxidation resistance of the zirconium alloy is needed. This fact is connected with the normal working of nuclear reactors and accidental conditions.

Coatings with 2.5 μm thickness and the composition of Zr40Si24Cr36 were obtained using the PVD method. During the autoclave test (360°C/195 bar/water simulating water used in PWR), the deposited Zr40Si24Cr36 layer protected the base material

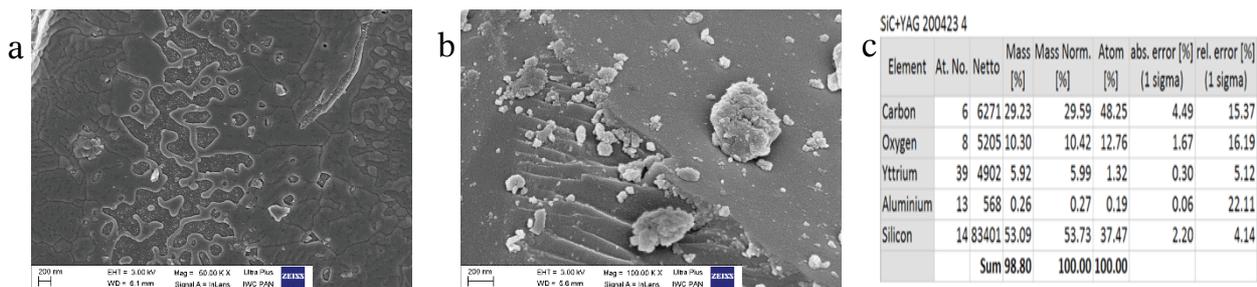


Fig. 3. SEM images of the coated SiC grains presented with different magnifications: (a) 50 000×, (b) 100 000×, and (c) obtained elemental composition of the material.

(here: Zry-2) from oxygen migration. The developed material Zr40Si24Cr36 can be considered as an oxidation protective layer for zirconium alloys.

The proposed, developed, and produced (SiC + YAG) powder is the main compound forming a protective layer on the Zr1Nb alloy using the SPS method. In the case of powder, a protective mechanism in the way of YAG oxidation is assumed to protect the SiC against decomposition at high temperatures. In the case of coating, the SiC coating will play a protective role for zirconium alloys as the thermal barrier coatings.

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