Archives of Materials Science and Engineering
Volume 77
Issue 2
February 2016
Pages 53-57
International Scientific Journal published monthly by the World Academy of Materials and Manufacturing Engineering

Modification of zirconium alloy surface using high intensity pulsed plasma beams

B. Sartowska [a] *, W. Starosta [a], M. Barlak [b], L. Walis [a]
[a] Institute of Nuclear Chemistry and Technology, ul. Dorodna 16, 03-195 Warszawa, Poland
[b] National Centre for Nuclear Research, ul. A. Sołtana 7, 05-400 Otwock-Świerk, Poland
* Corresponding e-mail address: b.sartowska@ichtj.waw.pl

ABSTRACT

Purpose: The aim of the research was to identify possibility of extending the life time of zirconium claddings. Materials used in nuclear reactors work in extremely hard conditions: irradiation, corrosion, stress. 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. In the case of loss-of-coolant accident (LOCA), the extremely fast oxidation of zirconium at steam or air/steam mixture at temperatures above 800°C results in intense hydrogen generation and possible hydrogen-oxide mixture explosion. The development of the solution to minimize the risk of the accidents mentioned above is urgently needed. The concept of Accident Tolerant Materials (ATM) has been developed recently.

Design/methodology/approach: Zirconium surface were treated with 30 high intensity pulsed plasma beams (HIPPB) Cr+Ar, Y+Ar or Al+Ar, with energy density of 4.0 J/cm^2. Oxidation tests: autoclave (water, 360°C, 19.50 MPa) for 7 and 40 days and oven (700°C and 800°C/1000 s/air) followed by cooling in water were performed. Samples were characterised with: SEMs, EDS and GXRD.

Findings: Zirconium samples with modified surface layer showed the higher resistance for oxidation in simulated conditions of normal work of PWR reactor and in elevated temperatures.

Originality/value: Carried out work was connected with new concept of development accident tolerant materials - ATM.

Keywords: Zirconium alloys; Corrosion in high temperatures; Electron microscopy; Surface treatment

Reference to this paper should be given in the following way:

B. Sartowska, W. Starosta, M. Barlak, L. Walis, Modification of zirconium alloy surface using high intensity pulsed plasma beams, Archives of Materials Science and Engineering 77/2 (2016) 53-57.

MATERIALS

1. Introduction

Zirconium, due to their good water corrosion and radiation resistance at normal working conditions of nuclear reactors is commonly used as cladding material for fuel elements. However, in the case of Loss of Coolant Accident – LOCA – conditions, the extremely fast oxidation of zirconium at steam atmosphere or and air/steam mixture at temperatures above 800°C results in intense hydrogen generation and possible hydrogen-oxide mixture explosion. These events, however very rare, negatively influence the public acceptance for nuclear energy. They also result in the high restoration costs of accompanying damages. The development of the solution to minimize the risk in such of accidents is urgently needed. The concept of Accident Tolerant Fuels (ATF) and Accident Tolerant Materials (ATM) – it means materials with increased accident tolerance – has been developed recently for this purpose [1,2].

Elemental composition of zirconium alloys used in nuclear reactors is present in Table 1.

Table 1.
Concentration of alloying elements in zirconium alloys (Zry) used for claddings (wt.%)

Alloy	Sn	Nb	Fe	Cr	Ni	O	Producer
Zry-2	1.50	-	0.13	0.1	0.06	0.12	Common used
Zry-4	1.50	-	0.21	0.1	0.007	0.12	Common used
M5		0.8-1.2					AREVA
ZIRLO	0.7-1.0	1.0					Westinghouse
E110	-	0.9-1.1					Russia

There are some methods and ideas for the increasing of claddings' corrosion resistance: (i) developing of new alloys with special composition and microstructure (for example: M5 from AREVA or ZIRLO from Westinghouse [3]), (ii) application of new materials resistant to water corrosion (for example: SiC [4]), (iii) modification of surface layer of Zry by so-called „Fresh-Green" process [5], (iv) modification of surface layer by irradiation with intense pulsed electron beam [6], (v) incorporation of rare earth elements to the surface of Zry [7], (vi) protective layer formed on the Zry surface (for example: on the base of silicon [8], ceramics MAX [9], FeCrAl alloys [10]).

The aim of the proposed research was to identify possibility of extending the life time of zirconium claddings and decreasing of the hydrogen gas generation. Authors proposed the application of high intensity pulsed plasma beams (HIPPB) for zirconium surface modification. Advantages of HIPPB method are: doping the high amount of dopants to the surface layer of target in the molten state, synthesis of unusual phase states due to high cooling rate, synthesis of gradient layers with depth dependent concentration of dopant.

2. Experiment

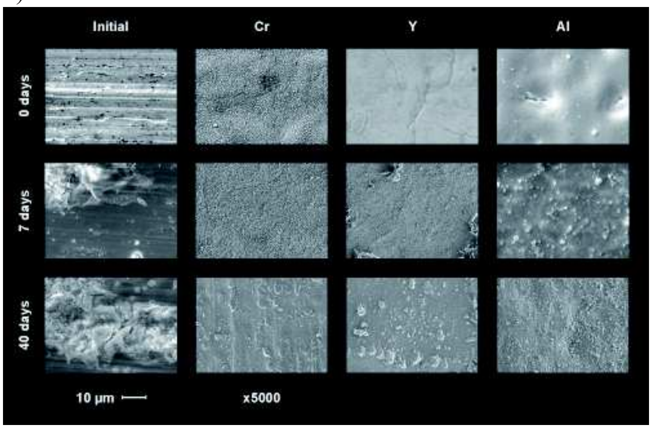
Zirconium sheet cold-rolled with thickness of 1 mm with elemental composition (% wt.): Zr – 98.29, Sn – 0.26, Fe – 0.21, Hf – 1.01 (Firmetal, China) was used for investigations. Samples were treated with 30 pulses of plasmas Cr+Ar, Y+Ar or Al+Ar, with energy density of 4.0 J/cm^2. Chosen elements were incorporated into the one surface of zirconium samples using high intensity pulsed plasma beams – HIPPB (10^6-10^8 W/cm^2). The plasma pulses were generated in a Rod Plasma Injector (RPI) described elsewhere [11]. The plasma pulses are formed at a low pressure, high-current discharge between two concentric sets of electrodes. A portion of the working gas is injected via high speed valve into the inter-electrode space. High voltage (HV = 25-35 kV) is applied between the outer/inner electrodes thus initiating discharge. Deposition by Pulsed Erosion – DPE mode of RPI operation was used. The beam contains ions/atoms eroded from ends of the electrodes as well as ions of the working gas. The pulse energy was high enough for melting the surface layer of material. The melt duration lasts in the µs range and the rapid solidification takes place. Corrosion tests were performed by two ways: in autoclave 4653 PARR (water, 360°C, 19.50 MPa – simulated conditions for normal works of pressurized water nuclear reactors type (PWR) for 7 and 40 days and in the oven 700°C and 800°C/1000 s/air followed by cooling in water. Samples of initial , modified and oxidised materials were characterized using: SEMs DSM 942 (Zeiss, Germany) and EVO MA10 (Zeiss, Germany) for surface morphology analyses, thickness and quality of modified layer determination with etched cross-sections (10%HF+65%HNO_3+H_2O), EDS with Quantax 400 (Bruker, Germany) for determination of the concentration of elements incorporated into the modified surface layer, GXRD (Bragg geometry, grazing angle of 5 degree) with Advance 8 diffractometer (Bruker, Germany) for phase identification and analysis.

3. Results and discussion

3.1. SEM observations

Results of SEM observations of initial, modified and oxidised in autoclave materials are present at Figure 1. Parallel scratches as the result of initial material production are clearly seen at the surface. After modification processes scratches disappeared. Cracks, craters and droplets of mixed material can be seen at the samples surfaces. All these features are characteristic for remelting techniques of the surface modification. Surface layer was remelted in all cases of used modification method (Fig. 1a, "0 days" line). Effects of surface layer oxidation are clearly seen at all samples after autoclave tests. In the case of 7 days test products of corrosion, craters and parts of corroded (oxidised) layer were visible at the initial material surface. All modified layers were uniform and compact. In the case of Y and Al elements used for modification small particles at the surface are visible. Layer modified with Cr incorporation looked like the best one (Fig. 1a, "7days" line). In the case of 40 days test surface layer of initial material was completely destroyed. Deep craters, corrosion pits and corroded area with particles of corrosion products were seen. Craters, corrosion pits and cavern at the sample modified with Cr were present. Particles of corrosion products at the surface of the sample modified with Y were visible. Surface after Al modification looked like the best one – without cracks, pits and corrosion products presence (Fig. 1a, (40 days" line). The thickness of modified layer were estimated as: 0.4 μm for Cr, 0.38 μm for Y and 0.35 μm for Al incorporation (Fig. 1b, "0 days" line). Thickness of the oxidised layers were determined as 1.37±0.04 μm and 2.47±0.08 μm for 7 and 40 days, Fig.1b "7 days" and "40 days" lines respectively. These results are with agreement with results presented in [12] where studies of Zircalloys corrosion processes were performed and discussed.

a)



b)

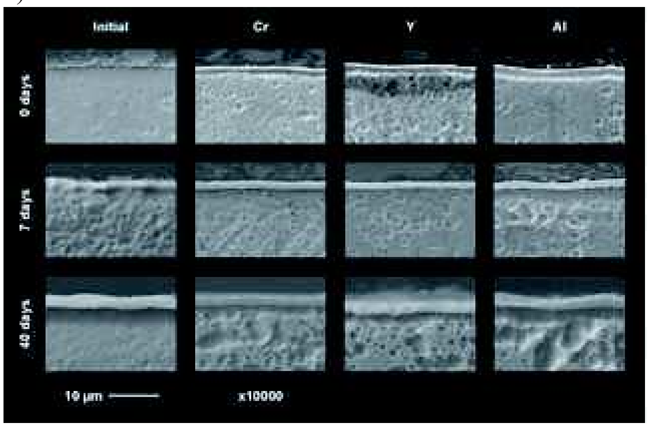


Fig.1. Results of SEM observations of initial, modified and oxidised materials a) surface, b) cross-sections

3.2. EDS analysis

Elemental concentration of elements incorporated to the surface layer as the result of modification processes were: Al – 10.0 at.%, Cr – 11.0 at.%, Y – 6.0 at.%. The range of accelerated with 20 kV electrons estimated with SUSPRE program was about 2 μm. Obtained data was from the whole thickness of modified layer and the base material.

3.3. Phase analysis

The X-ray diffraction patterns were collected at Bragg geometry and at grazing angle of 5 degree for initial and implanted samples after their oxidization in autoclave and for the samples oxidized in the oven. At this angle the diffraction patterns were collected from the surface layer up to depth of around 3 μm. The main phase observed in the surface layer of modified and oxidized samples was identified as monoclinic zirconium oxide (crystallographic space group $P2_1/c$ with parameters a=5.14630Å, b=5.21350Å, c= 5.31100Å, β=99.20°, ICDD 00-036-0420). The reflections from zirconium alloy lying beneath oxide layer area were also seen. However, their intensities in comparison to monoclinic oxide phase strongly depend on the treatment conditions. Small intensity broad reflections of tetragonal zirconium oxide phase were also identified.

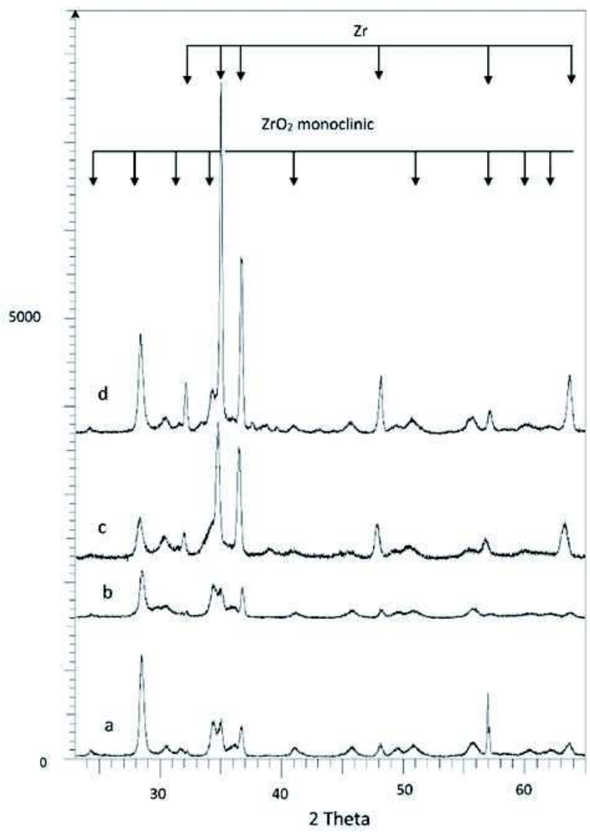


Fig. 2. The grazing incidence X-ray diffraction patterns of (a) initial and enriched with (b) Y, (c) Cr, (d) Al zirconium alloy samples after oxidation in air at 700°C/1000 s following by cooling in water

The X-ray diffraction patterns for initial and enriched with Y, Cr, Al samples after oxidation in air at 700°C/1000 sec are presented at the Fig 2. In the case of Al incorporated sample the intense zirconium alloy reflections can be observed. The smaller one are also seen in the case of Cr incorporated samples, while in the case of Y incorporated and the non-implanted sample they are absent. This shows that presence of Al in the surface layer influences on the oxidation kinetics at elevated temperatures. The same conclusions can be drawn for zirconium enriched with Cr, but in our experimental conditions this effect is smaller.

4. Conclusions

Modification of the surface layer of zirconium alloys were carried out using high intense pulsed plasma beams (HIPPB) with: 30 pulses of plasmas Cr+Ar, Y+Ar or Al+Ar, with energy density of 4.0 J/cm^2. Surface layer was melted and enriched with chosen element. Oxidation tests in: (i) autoclave with simulated condition of normal work of PWR nuclear reactors type (water, 360°C, 19.50 MPa) for 7 and 40 days and (ii) 700°C and 800°C/ 1000 s /air/ water cooled were performed. Zirconium samples with modified surface layer showed the higher resistance during autoclave tests as compared with initial material. Presence of Al or Cr in the surface layer influences the oxidation kinetics at elevated temperatures.

Authors suggest to carry out oxidation tests for the longer time for kinetics of oxidized layer growth investigation.

Acknowledgements

This work has been partially supported under IAEA Research Contract No. 19026/R0 and by Polish Ministry of Science and Higher Education under decision 3525/IAEA/2016/0.

References

[1] S.J. Zinkle, K.A. Terrani, J.C. Gehin, L.J. Ott, L.L. Snead, Accident tolerant fuels for LWRs: A perspective, Journal of Nuclear Materials 448/1-3 (2014) 374-379.

[2] R. Mariani, P. Medveedev, D.L. Porter, S.L. Hayes, J.I. Cole, X.-M. Bai, Novel Accident-Tolerant Fuel Meat and Cladding, Top Fuels September (2013) 15-19.

[3] P. Bossis, D. Pêcheur, K. Hanifi, J. Thomazet, M. Blat, Comparison of the high burn-up corrosion on M5 and low tin Zircaloy-4, Journal of ASTM International 3/1 (2006) 494-525.

[4] Y.H. Lee, T. McKrell, M.S. Kazimi, Safety of light water reactor fuel with silicon carbide cladding, Advanced Nuclear Power Program, MIT-ANP-TR-150, 2014.

[5] T. Sawabe, T. Sonoda, M. Furuya, S. Kitajima, M. Kinoshita, M. Tokiwai, Microstructure of oxide layers formed on zirconium alloy by air oxidation, uniform corrosion and fresh-green surface modification, Journal of Nuclear Materials 419/1 (2011) 310-319.

[6] I.P. Chernov, S.V. Ivanova, M.Kh. Krening, N. Koval', V.V. Larionov, A.M. Lider, N.S. Pushilina, E.N. Stepanova, O.M. Stepanova, Yu.P. Cherdantsev, Properties and structural state of the surface layer in a zirconium alloy modified by a pulsed electron beam and saturated by hydrogen, Zhurnal Tekhnicheskoi Fiziki 82/3 (2012) 81-87.

[7] X. Bai, J. Xu, F. He, Y. Fan, The air oxidation of yttrium ion implanted zircaloy-4 at 500°C, Nuclear Instruments and Methods in Physics Research B 160/1 (2000) 49-53.
[8] N. Chaia, S. Mathieu, F. Rouillard, M. Vilasi, The ability of silicide coating to delay the catastrophic oxidation of vanadium under severe conditions, Journal of Nuclear Materials 457 (2015) 124-129.
[9] M.W. Barsoum, MAX Phases - Properties of machinable ternary carbides and nitrides, Wiley-VCH Verlag GmBH, Weinheim, Germany, 2013.
[10] K.A. Terrani, S.J. Zinkle, L.L. Snead, Advanced oxidation-resistant iron-based alloys for LWR fuel cladding, Journal of Nuclear Materials 448 (2014) 420-435.
[11] Z. Werner, J. Piekoszewski, W. Szymczyk, Generation of high-intensity pulsed ion and plasma beams for material processing, Vacuum 63 (2001) 701-708.
[12] T.R. Allen, R.J.M. Konings, A.T. Motta, Corrosion of Zirconium Alloys, Comprehensive Nuclear Materials 5 (2012) 49-68.