ZIRCONIUM OXIDE COATINGS ON P91 AND ZIRCALOY (Zr-2.5%Nb) SUBSTRATES FOR USE IN SCWRs

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Abstract

The CANDU-SCWR presents difficult operating conditions for materials of construction and innovative methods, such as corrosion-resistant coatings, are being developed for reactor materials. In this study, Zircaloy (Zr-2.5%Nb) and P91 were coated with tightly adhering layers of zirconium-based oxides (ZrO_2 or Zr-NbO_2) through a plasma spray deposition (PSD) process. The coupons were exposed to deoxygenated supercritical water at 500^{o}C and 25 MPa for increasing durations, up to 900 hours. Coated coupons showed a reduced weight gain at all exposure times when compared to uncoated samples however SEM work reveals that poor coating adhesion resulted in degradation of the coating through oxide loss by spallation or dissolution processes.

Keywords: Materials, Corrosion, P91, Zircaloy, Coatings, CANDU-SCWR.

1. Introduction

The Generation IV International Forum (GIF) has been established to investigate future nuclear reactor technologies. This international treaty coordinates collaborations between government, academia and industry in several countries around the world. In Canada, two technologies are being considered: the Supercritical Water-cooled Reactor (SCWR) and the Very High Temperature Reactor (VHTR). While these designs differ in the heat transport system and coolant used, both present challenges in the areas of material selection, water chemistry and corrosion product transport. This work focuses on materials development for operation in the SCWR.

The CANDU-SCWR is a logical progression for the existing CANDU fleet. Researchers across Canada at universities and government labs (including Atomic Energy of Canada Limited (AECL), the Material Technology Laboratory of Natural Resources Canada (CANMET-MTL), and the National Research Council (NRC)) are working together to develop a potential design for the CANDU-SCWR. At the University of New Brunswick, materials and surface coatings are being investigated for use as coolant piping under the extreme conditions that exist in operating with supercritical water as a reactor coolant. There is some operational experience using SCW in fossil-fired power plants, however, differences in geometry and the lack of a radiation field make this experience of limited use. Additional work needs to be done in the

areas of chemistry control and corrosion product transport in SCW for the CANDU-SCWR to be a viable reactor technology.

There are a number of materials and surface treatments being considered as potential candidates for use in the extreme operating conditions that would be present in the CANDU-SCWR. Key material improvements being targeted include increased resistance to creep, general corrosion and stress corrosion cracking. The work presented here includes SCW exposure testing of Zircaloy (Zr-2.5%Nb), a zirconium alloy commonly used as pressure tube material in CANDU reactors, and P91, a ferritic-martensitic steel commonly used for steam piping in fossil plants. Zircaloy coupons were coated with a tightly adhering zirconium oxide (ZrO_2) film. Coupons cut from P91 plate were coated with a niobium-zirconium oxide. Both coatings were applied with a proprietary plasma-spray deposition (PSD) process prior to exposure in SCW. In the proposed CANDU-SCWR, subcritical light water coolant at 25 MPa enters the reactor core and leaves in the supercritical state at temperatures in excess of 625^{o}C; the coolant experiences a range of temperatures and densities while passing through the core. This work focuses on deoxygenated supercritical water exposure at 25 MPa and 500^{o}C.

2. Experimental

To conduct exposure tests of candidate alloys and surface coatings in supercritical conditions, a test loop has been assembled in the Department of Chemical Engineering at the University of New Brunswick. Figure 1 shows a piping and instrumentation diagram of the continuous flow system, which has a maximum flow rate of 500 g/min and can operate under a range of conditions in both the subcritical and supercritical ranges. Deionized water from a reservoir is pressurized with a positive displacement pump to a pressure of 25 MPa. The water is initially heated with fluid returning from the system using a tube-in-tube interchanger. The water is then heated through the critical point to the operating temperature of interest in the primary system heater; for this study, a temperature of 500°C was employed. The heated water then passes through a pressure vessel (autoclave) in which the test coupons are suspended from a coupon tree for exposure. Following the autoclave, the hot fluid passes back through the tube-in-tube interchanger where some of its heat is transferred to the incoming water. Before returning to the reservoir, the fluid is brought to ambient conditions by passing through a chilled water cooler and a back-pressure regulating valve.

Control systems are in place to monitor and regulate conditions within the system. Flow rate, temperature, pressure, oxygen concentration and conductivity are all recorded to a database using data acquisition software built in-house using Visual Basic. As-received test coupons were placed on trays suspended from a tree placed inside the autoclave,

Figure 2. These coupons were placed within the autoclave for increasing durations up to 900 hours to allow for SEM and weight change analyses to be carried out as a function of exposure time.

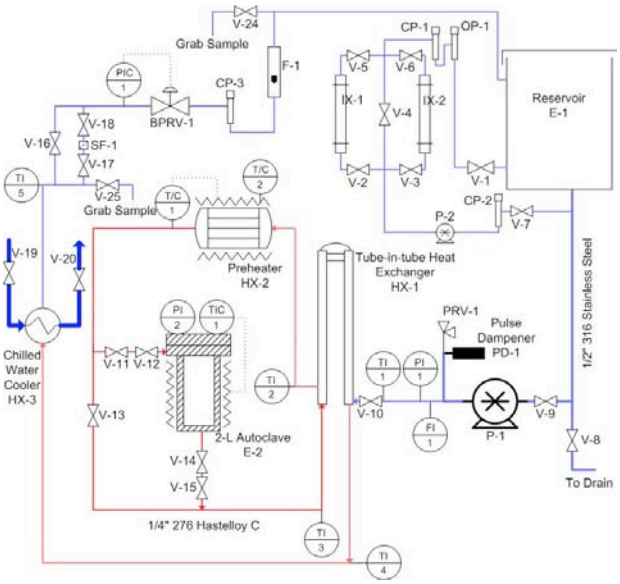


Figure 1- Schematic of UNB's SCW test loop.

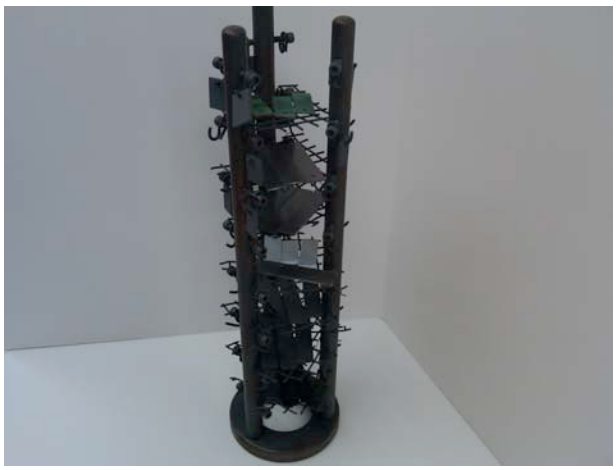


Figure 2- Coupon tree

Selected coupons of zircaloy and P91 were coated through a proprietary plasma spray deposition process at the NRC Institute for Fuel Cell Innovation and together with blank coupons of zircaloy and P91, and ZrO_2-coated Zircaloy coupons were exposed to SCW at 500^{o}C for increasing durations of 100, 250 and 500 hours. The two coupons of P91 coated with ZrO_2 were exposed for 500 hours followed by exposure for a further 400 hours on one of each coupon type, totalling 900 hours of exposure for select coupons. All of the coupons were weighed and dimensioned before and after exposure to get weight change information; additionally, all of the coupons underwent detailed surface characterization. For this experiment, the flow rate in the loop was fixed at 200 g/min with the dissolved oxygen concentration kept below 5 ppb as measured by an Orbisphere EC oxygen sensor in the water purification circuit.

The coupons were characterized pre- and post-exposure using scanning electron microscopy (SEM) at the Microscopy and Microanalysis Facility at the University of New Brunswick in plan view to evaluate the coating integrity. Secondary electron imaging (SEI) was performed on the coupons at increasing magnifications along with energy-dispersive x-ray spectroscopy (EDS) for compositional information.

3. Results and Discussion

For this experiment, all of the coupons were exposed in the loop at 500^{o}C for varying exposure times, up to 900 hours. Weight change measurements and coupon dimensions were collected at each time interval to evaluate the corrosion characteristics of the coatings with time. Scanning electron microscopy in plan view was performed on all the exposed sample and oxide compositions were evaluated through energy dispersive X-ray analysis (EDAX).

3.1 Zircaloy

The Zircaloy coupons experienced nearly linear weight gain with exposure time as seen in Figure 4 for all coupon types. More weight gain was measured for the blank Zircaloy coupons than for the coated ones, which would suggest that the PSD ZrO_2 coating offered some protection, at least initially, against oxidation. At the longest exposure time, 900 hours, the coated coupons experienced 30% less weight gain than the blank Zircaloy sample.

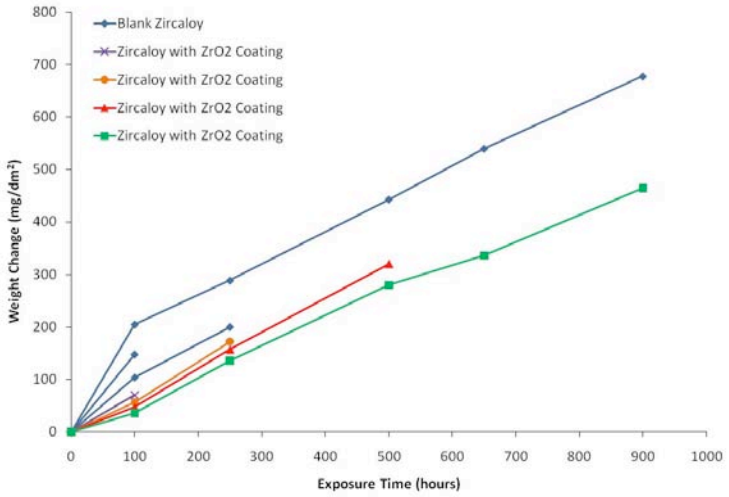
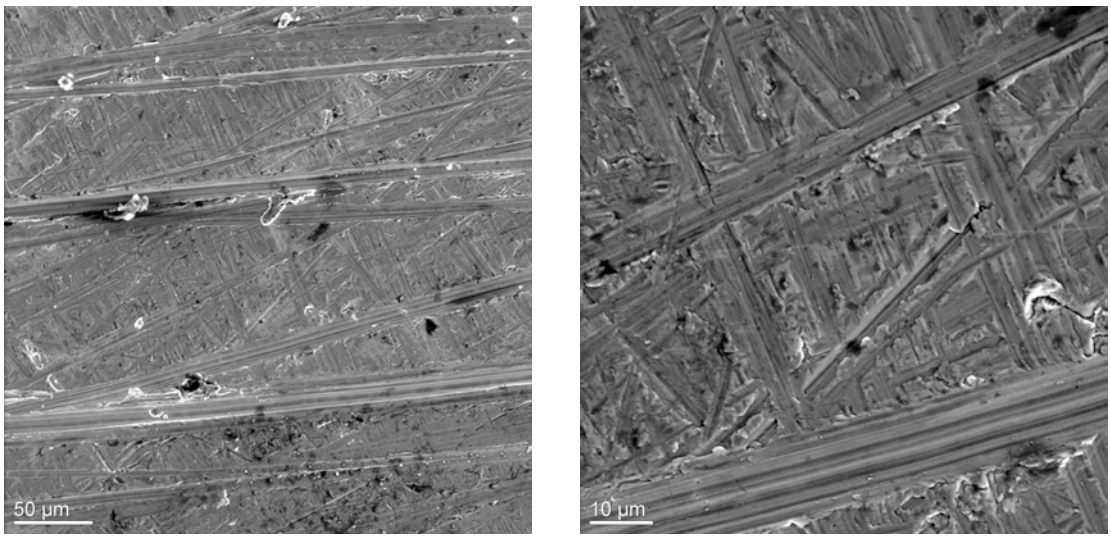
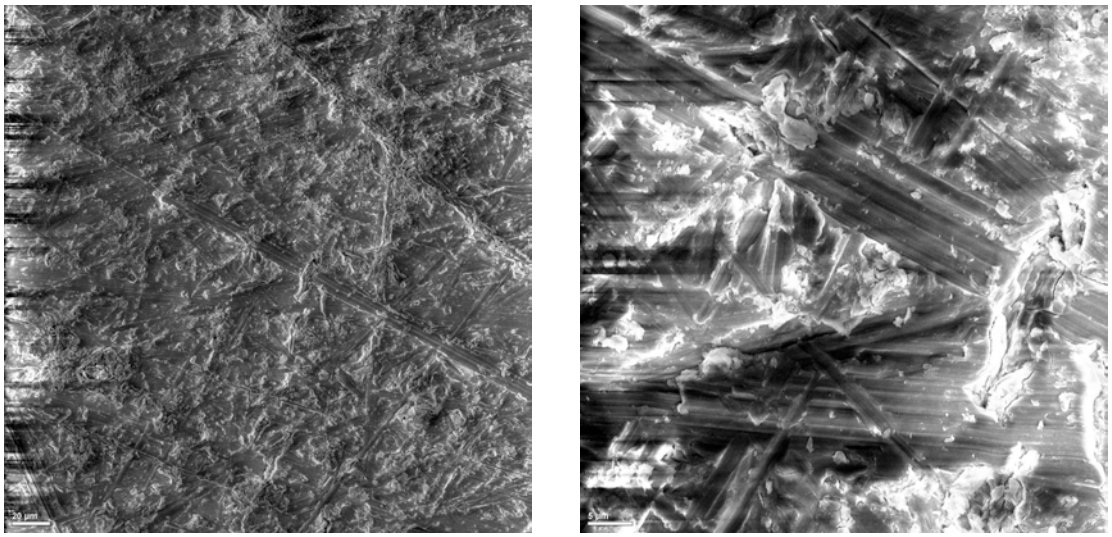


Figure 4- Blank and ZrO_2-coated Zircaloy exposed to SCW at 500°C and 25 MPa

The large weight gains observed on the Zircaloy coupons are supported with the SEM work. Zirconium oxides were formed on the surface of the blanks, which accounted for the weight gains measured. Figure 5 shows the two Zircaloy blanks before (a, b) and after (c,d) 900 hours of exposure to SCW at 500°C at increasing magnification. There is a clear difference in the surface finish after the samples were oxidized although the initial polishing lines are still visible on all surfaces.



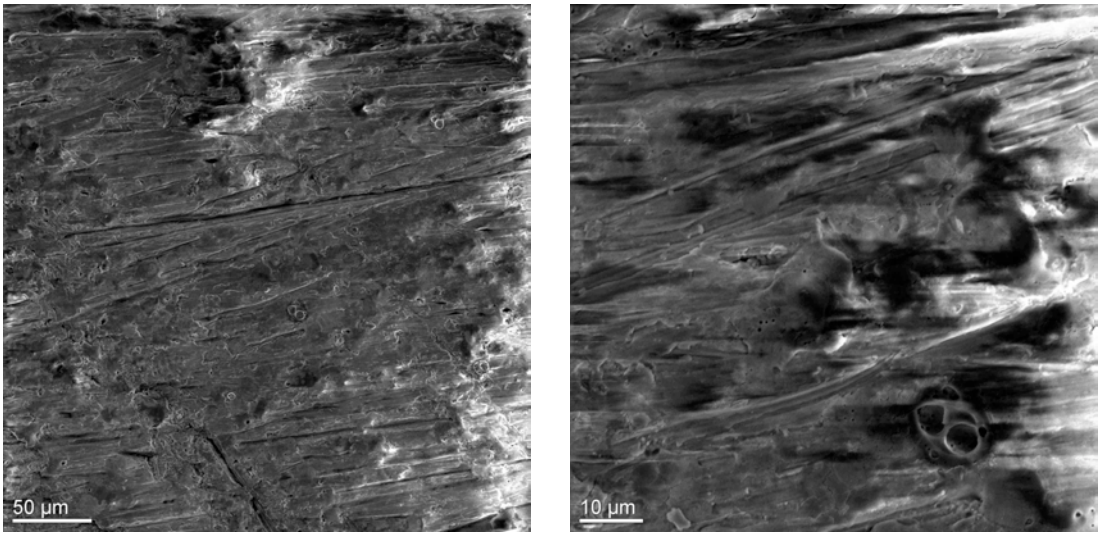
(a) (b)



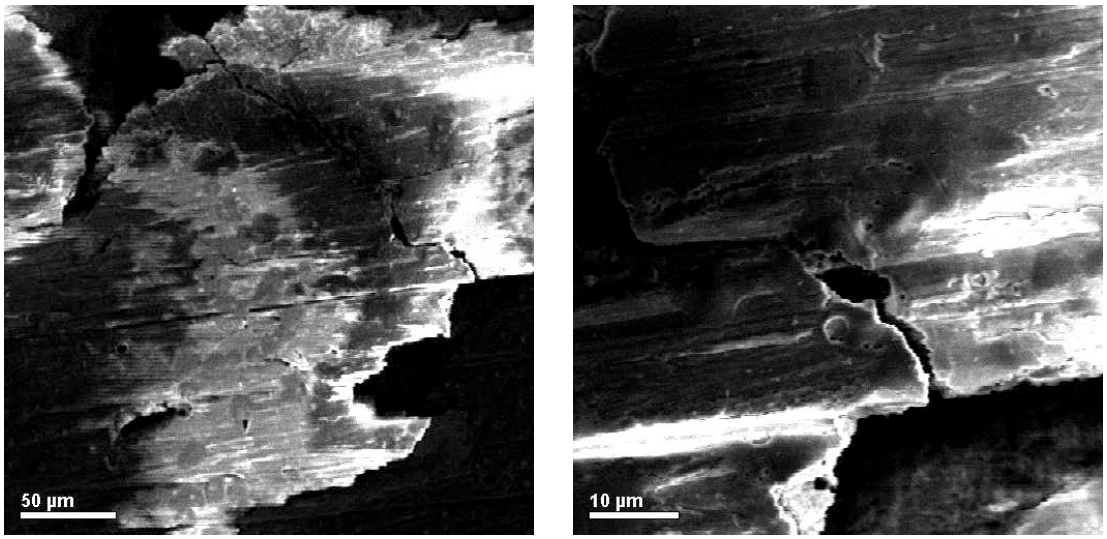
(c) (d)

Figure 5- Zircaloy blank coupons before (a, b) and after (c, d) exposure to SCW at 500^{o}C and 25 MPa for 900 hours.

Figure 6 shows the coated Zircaloy coupons before (a, b) and after (c, d) 900 hours of exposure. Pre-exposure SEM images show a continuous, non-porous ZrO_2 coating covering the entire surface with some indication of surface cracks. After exposure, the coating oxide appears significantly cracked with large flakes having been removed or delaminated from the surface. While some of the coating remains intact, large sections of the Zircaloy substrate have been subjected directly to the SCW environment thus creating a sub-coating oxidation that seems to be pushing off the original protective coating. The delamination of the ZrO_2 coating could have contributed to the weight change trend observed in Figure 4. The smaller weight gains observed for the coated samples could be a result of the loss of sections of the coating from the surface in addition to the protection provided in the initial exposure time over the uncoated samples.



(a) (b)



(c) (d)

Figure 6- Zircaloy coated coupons before and after exposure to SCW at 500°C and 25 MPa for 900 hours

3.2 P91

The P91 coupons experienced weight gains with time as shown in Figure 7; after high initial weight gains, the corrosion rate appears to stabilize and follow a linear trend that continues for the remainder of the experiment. Coated P91 coupons show less overall weight gain than their blank counterparts; this is mainly attributed to the protection provided in the early stages of exposure and oxidation. After approximately 250 hours of exposure, the slope of the weight change curve is identical for both the coated and blank samples indicating that the protective nature of the ZrO_2 coating only lasted for a short time. At 900 hours of exposure, the coated coupon had a weight change 33% less than the blank coupon.

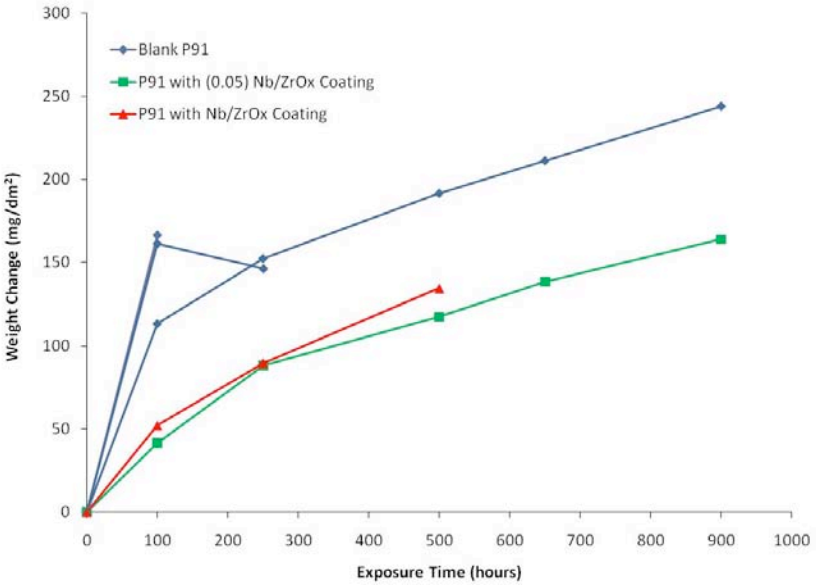


Figure 7- Blank and coated P91 exposed to SCW at 500°C and 25 MPa

SEM work for the blank P91 coupons supports the weight change results described above. Figure 8 shows high resolution images of blank P91 before (a,b) and after (c,d) 900 hours of exposure. Initially, the coupon surface was untarnished with polishing lines visible along the face. After exposure, a thick continuous layer of magnetite developed with a similar structure observed as has been seen in previous work on P91 and other ferritic alloys. This tubular magnetite morphology is interesting and is discussed in more detail elsewhere [1-4].

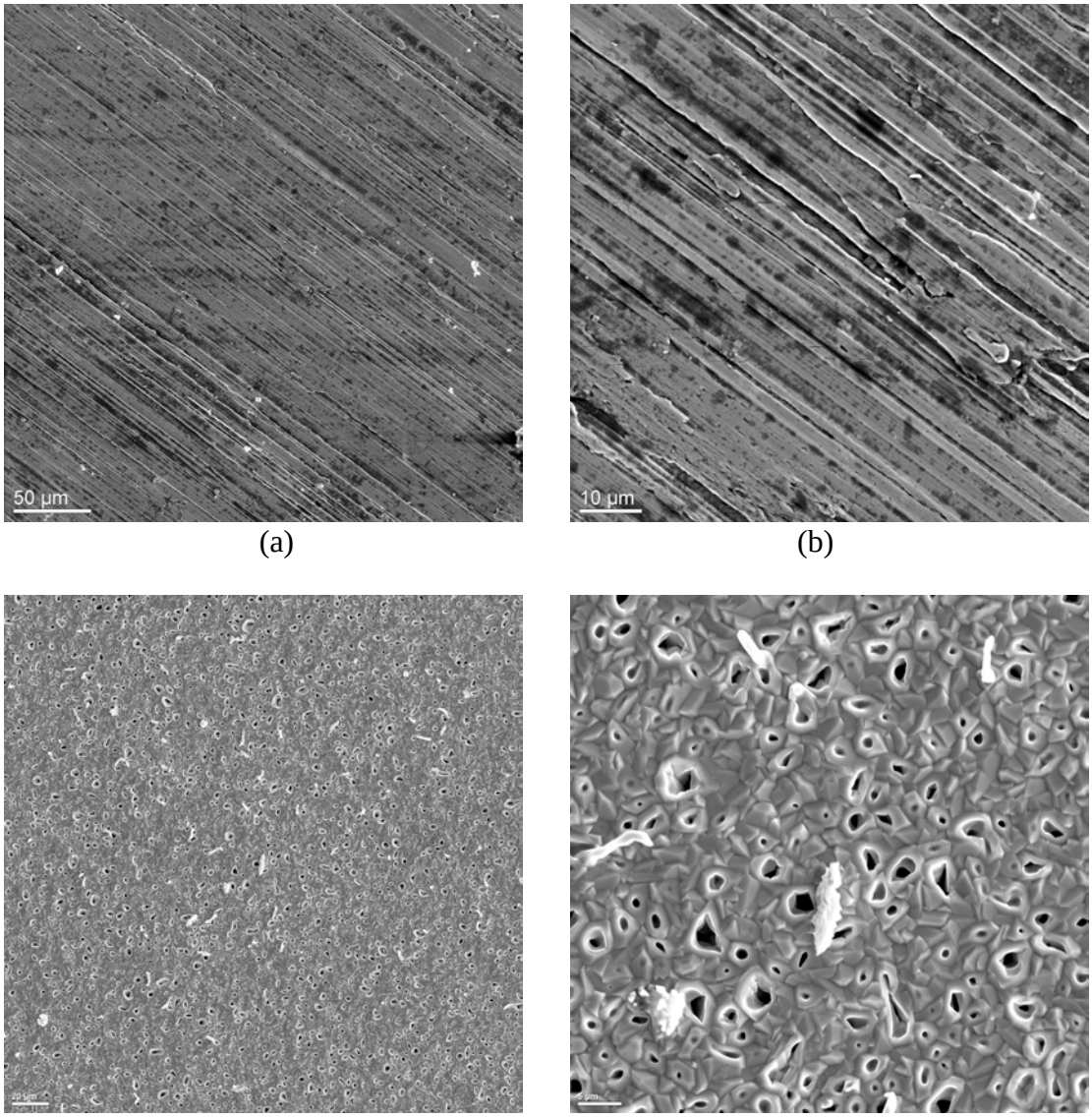


Figure 8- P91 blank coupons before (a, b) and after (c, d) exposure to SCW at 500^{o}C and 25 MPa for 900 hours.

Figure 8 shows SEM images of the coated P91 samples before (a, b) and after (c, d) 900 hours of exposure. Prior to exposure, a thick continuous coating of (0.05)Nb/ZrOx is observed covering

the entire surface. This coating has a scalloped, porous morphology and was thick enough to prevent detection of the substrate P91 with EDS analysis. The after exposure surface, Figure 9(c, d), resembles the blank, uncoated P91 surface shown in Figure 8 (c, d), with a continuous tubular magnetite film. It is apparent that the original coating has been completely removed; EDS of the surface after exposure shows no trace of the niobium and zirconium originally found in the coating.

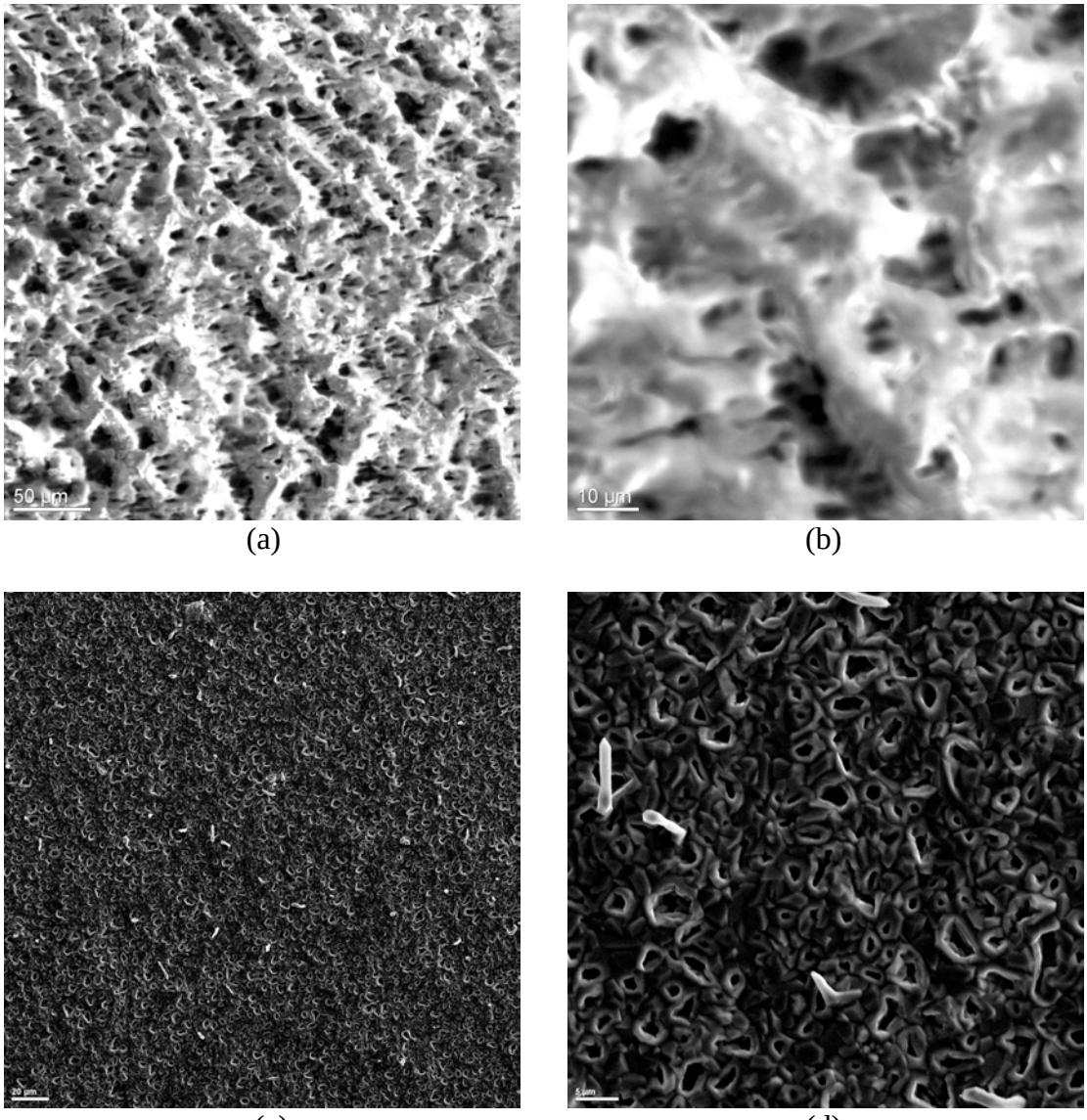


Figure 9- P91 coated coupons before and after exposure to SCW at 500^{o}C and 25 MPa for 900 hours

4. Conclusions

The study of advanced materials and surface coatings for use in next generation nuclear reactors, like the CANDU-SCWR, is necessary for the proposed designs to proceed. To achieve acceptable corrosion rates on conventional nuclear materials, research in the areas of alloy

design, coating design and coating application will need to converge. This work outlines a supercritical water exposure study on Zircaloy and P91 coupons coated with ZrO_2 and (0.05)Nb/ZrOx, respectively. Experiments were conducted using the supercritical water test loop at the University of New Brunswick. While weight change data for both coatings showed a reduction in weight gain of up to 30%, supporting SEM work shows the break down and instability in the coatings once exposed to SCW. After 900 hours, a zirconia coating on Zircaloy delaminated from the substrate and flaked off potentially due to oxidation of the base material below the coating, initiated through surface cracks in the coating. For the P91 coupons, there was no evidence that any of the original (0.05)Nb/ZrOx coating remained; the morphology of the oxide film that developed was identical to that of the blank P91 coupons. It is clear that the coatings do offer some protection in the early stages of oxidation but their degradation over short exposure periods allows oxidation to continue at the same rate as the uncoated samples; much more work is required to eliminate surface defects in the ZrO_2 coatings to prevent delamination and removal.

5. Acknowledgements

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6. References

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