Development of Ceramic Coatings for Metallic Components in Supercritical Water-cooled Reactors

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Abstract

A series of ceramic coatings have been prepared by spray pyrolysis processes on P91 substrates. Primary results show that coatings obtaining with different coating compositions and procedures can reduce the weight gain of P91 samples by factors of two to ten for exposure times up to 500 hours in deaerated supercritical water at 500^{o}C and 25 MPa. Results also show that the weigh gain of a P91 sample with Al_2O_3 coating is about nine times less that that of uncoated P91 after exposures for 400 hours in thermally deaerated supercritical water at 650 ^{o}C and 25 MPa. These results indicate that the Al_2O_3 coating shows promise for preventing oxidation of P91 alloy under supercritical water conditions.

Ceramic coatings on Zircaloy substrates have also been prepared using a plasma electrolytic oxidation process. After 400 hours of testing in SCW at 500 ^{o}C, the samples with ceramic coatings show improved corrosion resistance compared to the bare Zircaloy substrates.

1. Introduction

In recent years, due to the alarming increase in worldwide CO_2 emission, the route of large-scale energy production by CO_2 free nuclear fission reactors has become more and more attractive. The Generation IV international forum has, therefore, selected six innovative concepts for nuclear reactors based on safety and environmental issues [1]. One of the most promising advanced reactor concepts for Gen IV nuclear reactors is the supercritical water reactor (SCWR). Operating above the thermodynamic critical point of water (374 ^{o}C, 22.1 MPa), the SCWRs offer many advantages compared to current light water reactors (LWRs), such as the use of a single phase coolant with high enthalpy; the elimination of components such as steam generators, steam separators, dryers, and a low coolant mass inventory resulting in smaller components with much higher thermal efficiency (i.e., about 45% vs. about 33% efficiency for LWRs) as well as better fuel usage [2]. The SCWRs design fulfills the criteria of economics, safety and sustainability considered in the Generation IV International Forum. Unfortunately, accompanying the increased efficiency, supercritical water at higher operating temperatures and pressures is much more aggressive than the coolant in current water-cooled reactors, especially under very oxidizing environment. At high dissolved oxygen concentrations, the oxidation rate is significantly enhanced [3].

Typical materials for applications using high-temperature and high-pressure aqueous solutions are ferritic-martensitic stainless steels, nickel-based alloys, zirconium-based alloys, titanium, tantalum, noble metals, or ceramics [4,5]. Although metallic or alloy materials have the advantages of high mechanical strength and easy fabrication into complex shapes, these materials may be severely attacked under the operating conditions of SCWRs. Ceramic materials are known for their good resistance in corrosive environments, and are suggested as suitable reactor materials for supercritical water oxidation (SCWO) applications [6]. Hara et al. carried out a screening test of 18 kinds of ceramics, and demonstrated that oxide ceramics had better corrosion resistance than non-oxide ceramics in a SCW environment [7]. Boukis et al. measured the corrosion behavior of various ceramics in a simulated SCWO environment [8]. Their results showed that only a few Al_2O_3- and ZrO_2-based materials did not corrode severely in this very corrosive fluid. In comparison, HIP-BN, B_4C, TiB_2, Y_2O_3 and Y-TZP disintegrated; SiC- and Si_3N_4-based materials showed a large weight loss of up to 90 %. One obvious disadvantage of ceramics is that their mechanical strength is usually not sufficient for the practical applications. Advanced ceramic coatings combined with an alloy bond may offer properties that are suitable for use in a SCWR.

Spray pyrolysis deposition (SPD) is a cost-effective process to deposit films of a variety of materials [9]. The process involves atomizing a solution containing soluble salts of the constituent atoms of the desired compound, into discrete droplets and spraying the droplets onto a heated substrate. The sprayed droplets reaching the hot substrate surface undergo pyrolytic decomposition and form a chemical compound. The chemical reactants are selected such that the products other than the desired compound are volatile at the temperature of deposition and thus escape into the vapor phase. The substrate provides the thermal energy for the thermal decomposition and subsequent sintering of the constituent species giving rise to a coherent film. The main advantages of spray pyrolysis deposition include the simplicity of the apparatus, the low cost of the process and the ease of scalability to a large scale. National Research Council Canada's Institute for Fuel Cell Innovation (NRC-IFCI) has been developing spray pyrolysis technique for various applications since 2004. Processes for depositing various oxide films have been developed [10]. In this study, dense and well-bonded ceramic oxide layers have been successfully deposited on P91 substrates using spray pyrolysis and were examined in a SCW environment in an autoclave.

Plasma electrolytic oxidation (PEO), also called plasma electrolytic deposition, micro-arc oxidation, pulse plasma anodization, or spark anodization, is a novel method to produce hard and corrosion resistant ceramic coatings on Al, Mg, Ti, Zr, and other light metals as well as their alloys [11]. The PEO method utilizes the formation of micro-arc plasma discharges on the surface of the workpiece treated in an electrolytic aqueous solution. The resulting coatings are typically 10–50 μm thick with crystalline or amorphous phases containing metal and electrolyte constituents [12]. Properties of this multi-function protective ceramic coating include very high hardness, excellent wear resistance, excellent corrosion resistance, extremely high coating–substrate adhesion, high thermal shock resistance, and dielectric property. The excellent wear, friction, corrosion, and thermal properties of these coatings are of particular interest in textile machines, aerospace components, gas/oil extraction and refining machinery, and nuclear power plants. In this study, dense and well-bonded zirconia coating has been successfully formed on Zircaloy substrates using plasma electrolytic oxidation and examined in SCW environment in an autoclave.

2. Experimental section

Commercial P91 plate (American Alloy Steel, Inc.) and Zircaloy bar (Zr2.5Nb, ATI Wah Chang) were cut into samples with dimensions of 50 mm × 10 mm ×1 mm. Prior to the SPD and PEO treatments, the specimens were polished with 400 grit SiC abrasive paper, and degreased with acetone and then rinsed with deionized water.

In this experiment, spray pyrolysis deposition technique was utilized to deposit a dense coating of metal oxides on pre-cleaned P91 stainless steel substrates. In pneumatic spray deposition (PSD) process, a compressed gas was utilized to atomize and spray a precursor solution; in integrated PSD and electrostatic spray deposition (ESD) process, an electrostatic field and a compressed gas are both applied to atomize and spray a precursor solution.

In order to get dense coatings for corrosion protection, laboratory experiments were carried out to find the optimized deposition conditions. Organic solutions containing $Al(NO_3)_3$, $(NH_4)_2Ce(NO_3)_6$ plus tantalum isopropoxide, and $Mg(NO_3)_2$ plus Zr n-butoxide n-butanol complex were prepared to provide precursors for Al_2O_3, $(Ta_2O_5)_{0.04}(CeO_2)_{0.96}$ and $(MgO)_{0.01}$ $(ZrO2)_{0.99}$ coatings, respectively. The pH of the $Al(NO_3)_3$ solution was adjusted by $NH_3.H_2O$. Precursors containing multi metal elements were prepared according to the stoichiometric ratios of the metal oxides. The substrate temperature was around 600°C for Al_2O_3 coating and 650°C for the others. The detailed experiment conditions and the thickness of the obtained coatings are listed in Table 1.

Table 1. Experiment conditions for spray pyrolysis deposition

Sample	Coating Composition	Coating Thickness (μm)	Deposition Conditions		
			Method	Substrate Temperature (°C)	pH of Precursor Solution
S1	Al_2O_3	5	PSD	600	2
S2	Al_2O_3	5	PSD	600	3.5
S3	$(Ta_2O_5)_{0.04}(CeO_2)_{0.96}$	2.5	PSD	650	N/A
S4	$(MgO)_{0.01}$ $(ZrO_2)_{0.99}$	2.5	PSD	650	N/A
S5	Al_2O_3	5	PSD+ESD	600	2

Plasma electrolytic oxidation was utilized to form a dense ceramic coating on Zircaloy substrate. For plasma electrolytic oxidation, an appropriate pulsed power source developed by NRC-IFCI was used for the PEO treatment of the samples. The PEO unit mainly consists of a water-cooled glass electrolyser with stainless steel liner and a high power electrical source. The stainless steel liner also serves as the counter electrode. The electrolyte solution in this study is an aqueous solution consisting of 14 g L^{-1} sodium silicate (Na_2SiO_3). After the treatment, the coated samples were rinsed with deionized water and dried in air.

The pulse duty ratio is defined as follows:

$$\text{Duty ratio } (D) = \frac{t_{on}}{t_{on}+t_{off}} \times 100\% \qquad (1)$$

where t_{on} is the pulse on-time and t_{off} is the pulse off-time. In this study, the duty ratio of the negative pulse (D_{n}) was set as 10%; negative pulse voltage U_{n} was fixed at 50 V; the number of negative pulses was 1, i.e., a cycle of three positive pulses was followed by one negative pulse. The duty ratio of the positive pulse (D_p) and the positive/negative pulse proportion (R) were set 20% and 3, respectively. At the early stage of this process, a constant current mode was used at an average current density of 0.05 A cm^{-2}. The positive pulse voltage U_{p} was gradually increased with the build-up of films, and it reached 520 V after about 20 minutes. Then the constant voltage was maintained for further oxidation. The total time for PEO treatment was 7 h.

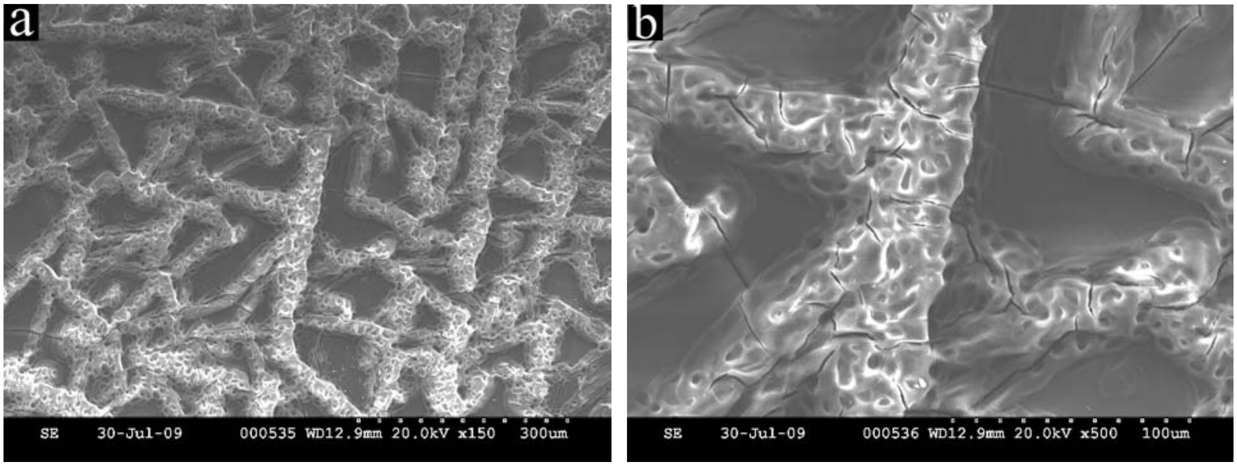
The phase composition of coatings was examined by X-ray powder diffraction performed on Bruker AXS D8 Advance with Cu K_α radiation. The morphology of the surfaces and cross-sections of the coatings was characterized using a scanning electron microscope (SEM, Hitachi S-3500N, Japan). Prior to the SEM examinations, the samples were coated with gold by sputtering to minimize charging effects under SEM imaging conditions. Chemical compositions and elemental distributions were analyzed by X-ray energy dispersion spectroscopy (EDS) coupled to the SEM (Oxford, UK).

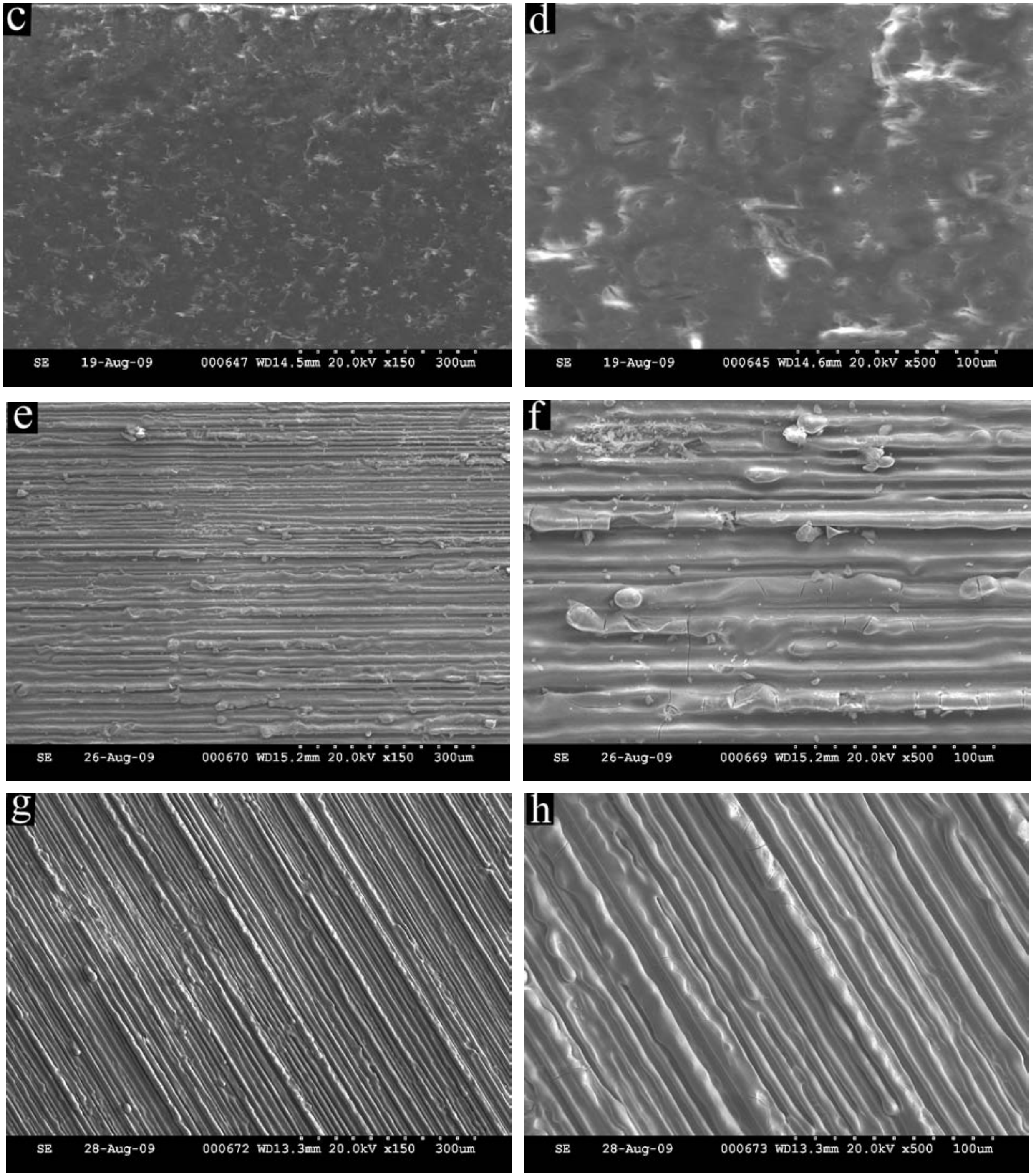
The autoclave testing was carried out collaboratively with the University of New Brunswick and Shanghai JiaoTong University. The P91 based samples were mainly tested at University of New Brunswick; the test conditions were 500°C, 25 MPa, pure de-ionised water pH~7 at room temperature, dissolved oxygen concentration (DO) <20 ppb. The Zircaloy based samples were tested at Shanghai JiaoTong University; the test conditions were 500°C, 25 MPa, DO<5ppb, without dissolved hydrogen. The P91 with Al_2O_3 coating was also tested at Shanghai JiaoTong University, the test conditions are 650°C, 25 MPa, DO<2ppb, saturated DH about 1.5 ppm, water flow rate about 0.8 liter/hour.

3. Results and discussions

3.1 Characterization of ceramic coatings on P91 prepared by spray pyrolysis deposition

Figure 1 shows the SEM images of the surfaces of the coatings. The coatings with different compositions show various morphologies due to the diverse behaviours of nucleation and growth of oxide materials. The coatings were dense but there are some shallow micro-cracks on the top of the Al_2O_3 coating (Figure 1a and 1b). A coating was gradually built up during the deposition by the repeated movement of the spray nozzle. Due to the repetitive nature of the process, when shallow micro-cracks form on the top of a coating during a spray run, the next run would fill the cracks. Therefore, such shallow micro-cracks were not a problem for obtaining dense coatings. The thickness of as-deposited oxide coatings is 2~5 μm, as listed in Table 1.

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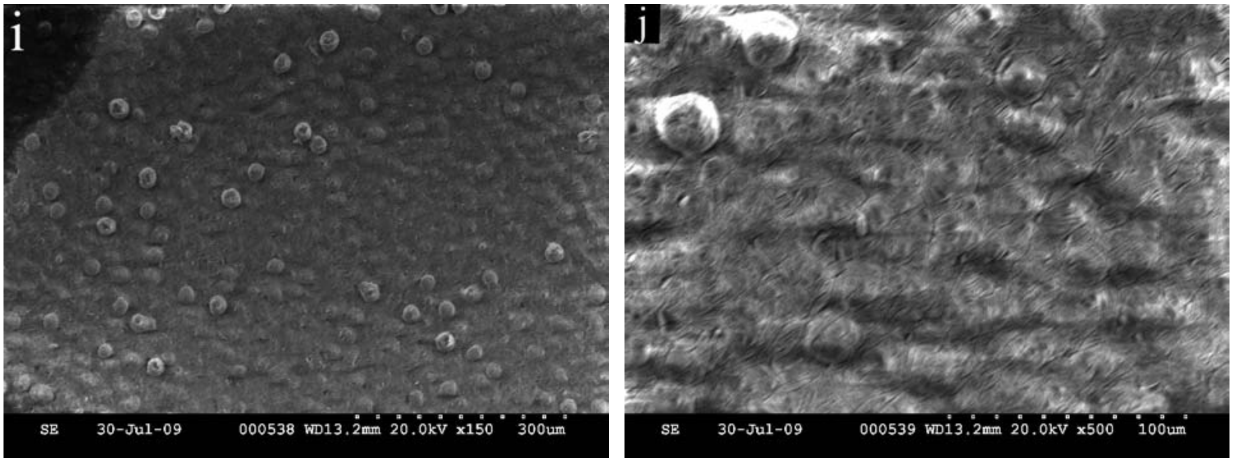


Figure 1. Surface SEM images of the coatings on P91 prepared by spray pyrolysis: (a, b) Al_2O_3 (c, d) Al_2O_3; (e, f) CeO_2-Ta_2O_5; (g, h) ZrO_2-MgO; and (i, j) Al_2O_3 . The grooves in e, f, g, h were the original machining grooves on the substrates. Because the roughness of these substrates was greater than the coating thickness, the coatings replicated the grooves, rather than covering them.

Oxidation is a common corrosion mechanism for many alloys in SCW environments [5]. We studied the effect of several coatings on the corrosion properties of P91 exposed to supercritical water at 500°C and 25 MPa with a dissolved oxygen concentration below 20 ppb for exposure time up to 500 h. As shown in Figure 2, the weight gains due to oxidation in P91 with Al_2O_3 and ZrO_2-MgO are smaller than that of bare P91 coupon. For the case of P91 sample with CeO_2-Ta_2O_5 coating, no obvious difference is observed compared with that of the P91 substrate.

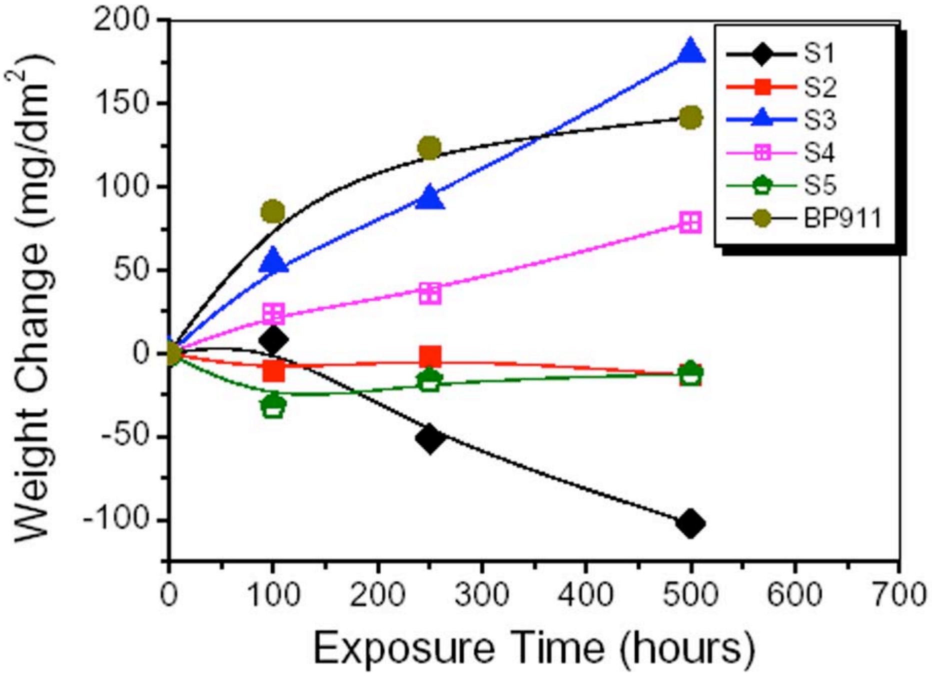


Figure 2. Weight gain versus time for the blank P91 substrate (BP91-1) and P91 with different coatings prepared by spray pyrolysis method: (S1) Al_2O_3; (S2) Al_2O_3; (S3) CeO_2-Ta_2O_5; (S4) ZrO_2-

MgO; and (S5) Al_2O_3, and exposed to supercritical water at 500°C, 25 MPa, and DO concenration <20 ppb in an autoclave

P91 samples with an Al_2O_3 coating prepared using the same conditions as those of S1 were also tested at Shanghai JiaoTong University at a higher temperature and lower DO concentration. As shown in Figure 3, the weight gain of the coated P91 sample is about 9 times less than that of the uncoated sample during a 400 h tests. This result also indicates that P91 with an Al_2O_3 coating has superior resistance at higher temperatures in SCW environment.

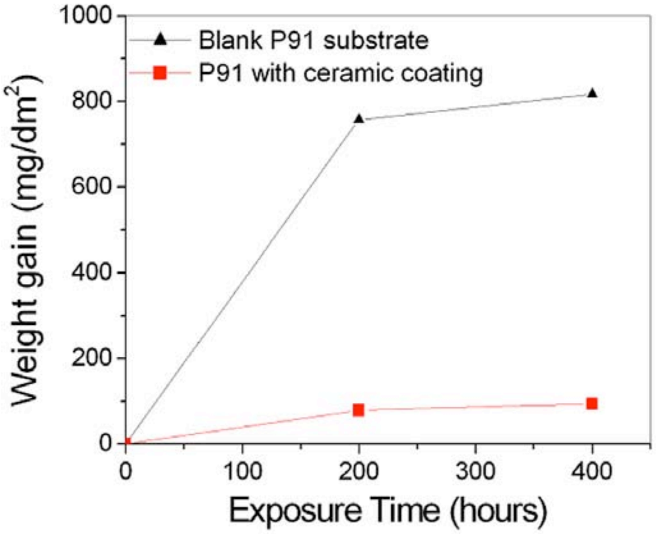


Figure 3. Weight gain versus time for the blank P91 substrate and P91 with an Al_2O_3 coating prepared by spray pyrolysis and exposed to supercritical water at 650°C, 25 MPa, and DO concentration <2 ppb in an autoclave

3.2 Characterization of coatings on Zircaloy prepared by plasma electrolytic oxidation

The phases of the coating material were characterized by XRD. Figure 4 shows the XRD patterns of the Zircaloy sample with coating and the bare substrate. Compared with that of Zircaloy substrate, the main phase of sample with coating is Baddeleyite-type ZrO_2 (JCPDS No. 37-1484). No peaks from the substrate were observed. It indicates that the coating is thick and crack-free.

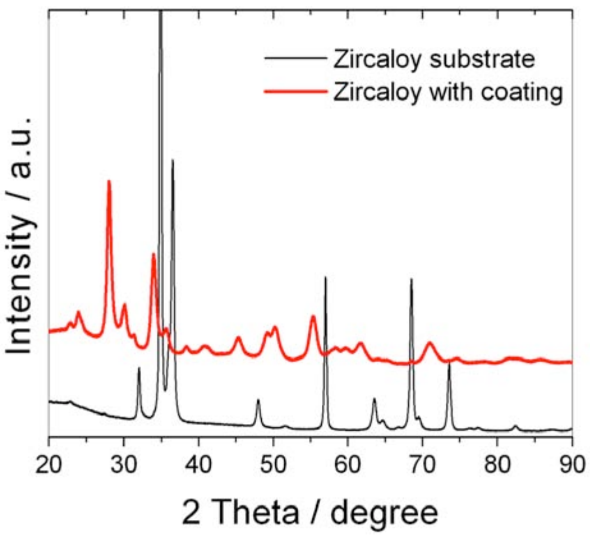
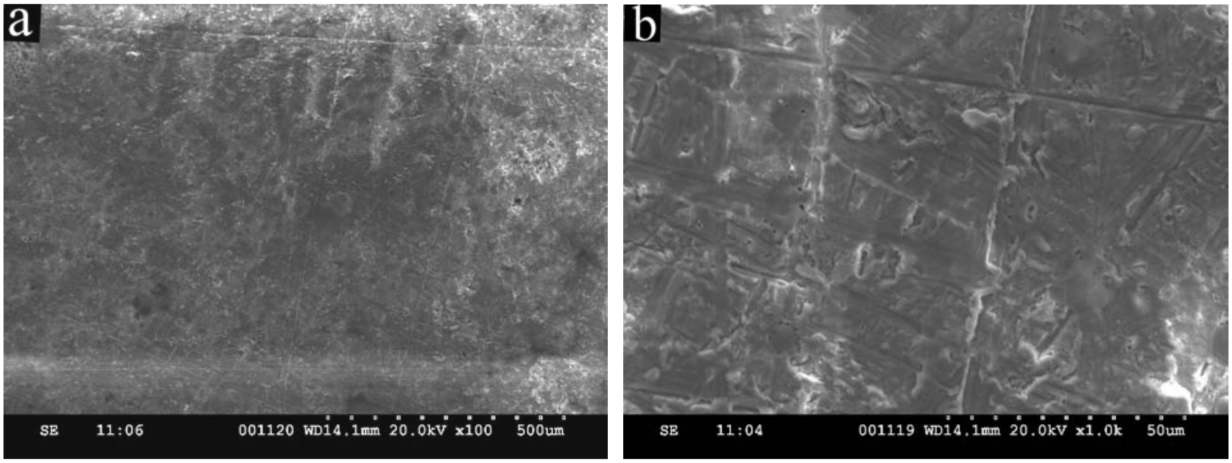


Figure 4. XRD patterns of the Zircaloy substrate and the coated sample. Coating conditions are at 2700 Hz, D_p = 20%, and R = 3

Figure 5a and 5b show the surface of the coating prepared at 2700 Hz, D = 20%, and R = 3. It can be seen that at this magnification the coating appears dense and crack-free. Figure 5c and 5d show cross-sectional SEM images of the coating. They show that the coating is continuous and uniform (Figure 5c). From the high-magnification SEM image (Figure 5d), it can be seen that the coating is composed of a multi-layer structure, which suggests that the coating grows layer by layer. The total thickness of the as-deposited oxide coating is about 30-40 µm. The thickness of a single layer is about 1-2 µm.



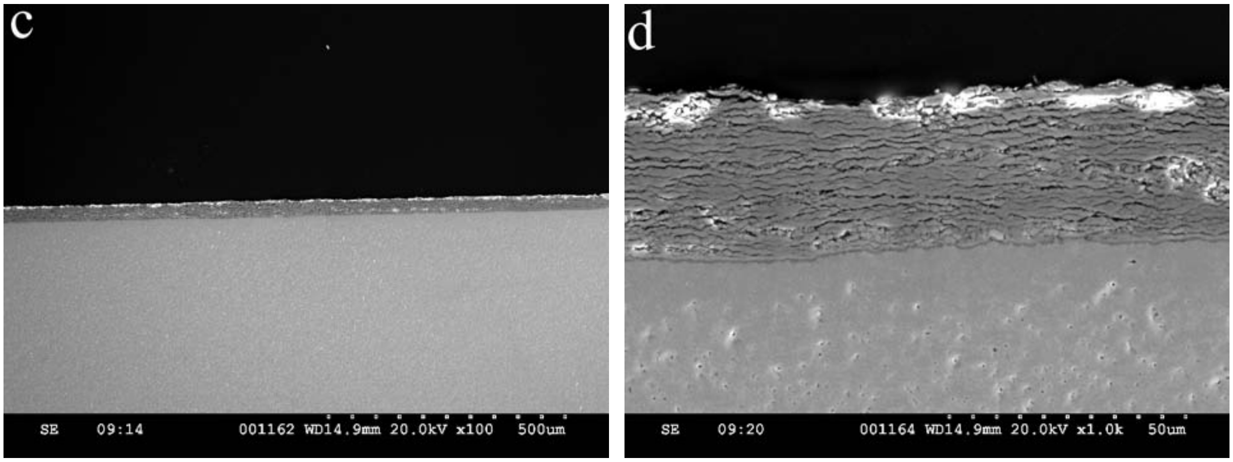


Figure 5. Surface SEM images (a,b) and cross-sectional SEM images (c,d) of the coatings formed on Zircaloy by plasma electrolytic oxidation

The corrosion resistance of the coated Zircaloy was studied by exposing the samples to supercritical water at 500°C and 25 MPa with a DO concentration below 5 ppb. As shown in Figure 6, the weight gain due to oxidation of the coated Zircaloy is about 1.5 times less than that of uncoated Zircaloy coupon for exposure times up to 400 h. The testing at longer exposure time is still on going.

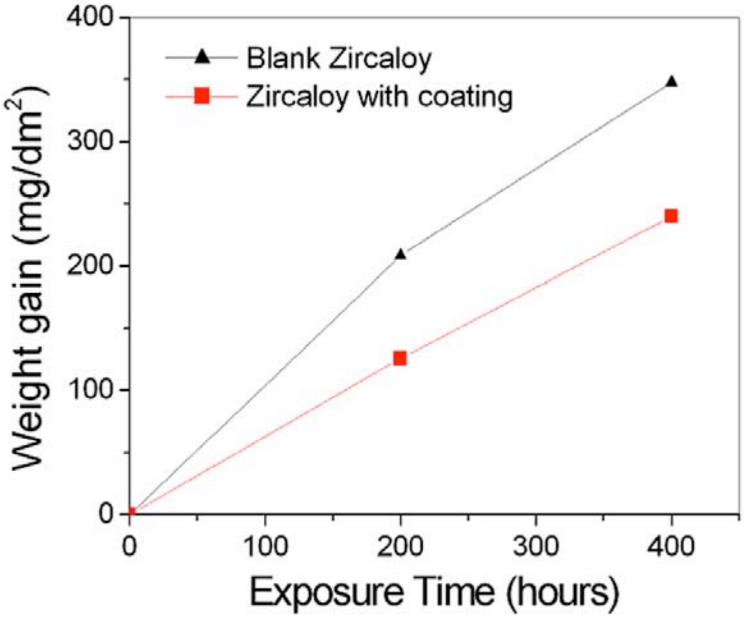


Figure 6. Weight gain versus time for the Zircaloy substrate with and without coatings prepared by plasma electrolytic and exposed to supercritical water at 500°C, 25 MPa, and DO concentration <5 ppb in an autoclave

3. Conclusions

Thin and dense ceramic oxide coatings have been deposited by spray pyrolysis on P91 substrates as protective coatings. At 500 °C and 25 MPa, and DO concentration <20 ppb in autoclave, the

Al_2O_3 and ZrO_2-MgO coatings were stable and were effective resisting oxidation in an SCW environment. In particular, P91 without Al_2O_3 coating is a promising candidate material for SCWR applications. Further studies will involve the characterization of the microstructure of the coatings and the optimisation of the coating thickness to ensure sufficient corrosion resistance under the expected SCW environment. Dense ZrO_2 coatings were formed successfully on Zircaloy substrates using a plasma electrolytic oxidation method. The coated Zircaloy samples showed better corrosion resistance than bare substrates in autoclave testing. Further studies will focus on studying systematically the effects of processing parameters and electrolyte solution on the microstructures and the property of resistance to corrosion. The demonstrated superior corrosion-resistant properties of P91 or Zircaloy with ceramic coatings in SCW environments compared with those of pristine substrates may open up a new avenue for the engineering of SCW reactors.

Acknowledgment

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