An Experimental Investigation on the Role of Gamma Radiation on Zirconium Alloy Corrosion using Electrochemical Techniques

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Abstract

Gamma radiation is suspected of playing a contributing role in accelerating the post-transition corrosion kinetics of zirconium (Zr) alloys in nuclear reactors. As it is difficult to isolate the independent effects of neutron and gamma radiation on in-reactor corrosion processes, previous work has so far only compared different reactors, or different regions of a reactor, to show instances where increases in gamma flux relative to neutron flux levels have led to enhanced corrosion rates. In an effort to definitively determine whether gamma radiation does enhance Zr alloy corrosion, and to quantify the effect of gamma dose and dose rate, electrochemistry tests have been performed using a mini-autoclave situated in the Co-60 gamma irradiator at the Dalton Cumbrian Facility. Such a facility enabled gamma-only exposures at dose rates of 37 Gy min^{-1} and 28 Gy min^{-1}. The use of the mini-autoclave permitted testing with equivalent PWR water chemistry conditions, at three different temperatures (150, 200 and 260 °C). Testing was conducted using Zircaloy-4 and Zr-2.5Nb working electrodes with both pre-transition and post-transition oxide films and the corrosion processes were monitored using open circuit potential measurements. The results support the hypothesis that gamma radiation produces an excess of charge-carriers within the oxide, which enhances corrosion at post-transition conditions. Nevertheless, in Zr-2.5Nb, the magnitude of the oxidising/anodic potential was lowered, considered to be a result of niobium doping.

1. Introduction

Research on irradiation-enhanced corrosion in Zirconium (Zr) alloys has predominantly focussed on the effects of neutron flux. Due to accurate quantification of neutron fluxes being required for the safe operation of a nuclear reactor, it is usually possible to correlate the experimentally observed in-reactor corrosion rates with the large amount of available neutron data. Neutron irradiation damages both the metal and the oxide, which is known to enhance corrosion kinetics within the core [1]; neutron damage knocks atoms from their lattice sites, developing interstitial and vacancy loops within the metal which promote irradiation hardening and support stress-free inward growth of the oxide, as well as leading to dissolution of second phase precipitates (SPPs) and redistribution of alloying elements [2]. However, studies that aim to isolate these effects, by pre-damaging the metal and/or oxide and then corroding the material in an autoclave, only observe a factor of 2 acceleration compared to non-irradiated samples [3], and therefore do not replicate the large accelerations, ~30 to 40 times higher, observed in-reactor [1]. Therefore, enhanced corrosion may not only be caused by microstructural damage, but by a combination of in-situ synergistic irradiation effects.

Since neutrons may not be the only sole contribution for irradiation-enhanced corrosion, other forms of irradiation have been considered. Within a reactor core the fuel cladding is not only exposed to neutrons, but fissions within the fuel also generate gamma radiation, fission fragments, beta particles and neutrinos. Some of these fission products are unlikely to affect corrosion, such as fission fragments and beta particles, which are contained within the fuel; or neutrinos, which tend to have little interaction with matter. However, it is possible that the high gamma irradiation flux experienced throughout the cladding could contribute to accelerating the corrosion process within thicker post-transition oxide films with fossil (porous) layers [4] [5] [6] [7] [8] [9].

It is difficult to independently assess the effect of gamma flux has on in-reactor corrosion since gamma rays and neutrons arise, for the most part, from the same originating process (i.e. the fissioning of nuclear fuel). Nevertheless, Rishel et al. were able to use electrochemical cells to assess the role of gamma radiation in reducing corrosion resistance, by comparing regions with different gamma-to-neutron

radiation compositions [4]. Furthermore, in a later study, Rishel and Kammenzind compared weight gain measurements between two different reactors, the Halden test reactor and the Advanced Test Reactor (ATR), which have different gamma-to-neutron flux ratios in the core due to differences in reactor design [4]. In addition, they also compared corrosion behaviour at different regions within the ATR, which showed a variation in gamma-to-neutron flux due to attenuation of neutrons in the coolant water, meaning non-fuelled regions generally had a much higher gamma-neutron ratio [4]. By plotting the results against gamma-to-neutron flux ratio, they found a trend in the data that revealed gamma radiation enhances the in-reactor corrosion behaviour of Zircaloy-4 [4]. Gamma radiation is thought to play this important role due to the specific n-type semiconducting properties of the barrier zirconium dioxide (ZrO_2) and the potential for charge carriers to enhance heterogeneous radiolysis at oxide-water interfaces, as explained by Rishel and Kammenzind in [5]. Gamma radiation is able to interact with the corrosive film layer because ZrO_2 has the properties of a wide-gap n-type semiconductor, with a relatively large band gap of ~ 5eV [7], meaning absorption of photons (gamma rays) can produce an excess of electron-hole pairs (excitons) [9]. These excitons have enough energy to degrade the protective oxide, leading to open porosity and accelerated corrosion rates [9].

To understand the role of gamma radiation on the corrosion of Zr alloys a test program was set-up at the Dalton Cumbrian Facility (DCF), which used electrochemical techniques to measure corrosion of Zircaloy-4 at different temperatures and dose rates in a gamma-only radiation environment. This was achieved using a recirculating autoclave which was custom designed to sit inside a Co-60 gamma irradiator, with feedthroughs for electrochemical measurements, for online monitoring of long-term corrosion tests as a function of both dose rate and corrosion temperature. The results are discussed in the context of improving in-reactor corrosion predictions.

2. Methods

The samples used in this study were made from fully recrystallized alpha-annealed Zircaloy-4 (Zr-4) and Zr-2.5Nb with two sets of oxide thickness; a set with a pre-transition oxide film thickness ~ 1 μm, and a set with a much thicker post-transition oxide with a thickness ~ 50 μm. These samples underwent Electrical Discharge Machining (EDM) to produced paddle-shaped working electrodes with a sample size of approximately 0.7 x 0.4 mm. The Zr-4 coupons were then tungsten inert gas (TIG) welded to 1/16" Zr-4 wire to allow individual electrochemical measurements to be performed on each specimen. The PWR coolant conditions were achieved in-situ during the gamma irradiation using a custom-made mobile High Temperature High Pressure (HTHP) recirculation loop and mini-autoclave system at the DCF, as part of the University of Manchester. In this experiment temperatures of 150, 200 and 260°C were used. The water chemistry, which was consistent of typical PWR requirements, created a reducing environment, which was maintained using H_2 overpressure. The reducing environment was achieved by initial degassing of the water with argon, followed by hydrogenating the system when the dissolved oxygen level was below 5 ppb. Hydrogenation was achieved using 10% H_2 in an Ar gas mix, fed into the system at 2 bar(g) overpressure, to give approximately 5 cc/kg concentration of H_2 in the loop. The Hastelloy C276 autoclave was placed in the centre of a Co-60 gamma irradiator. The gamma dose during all experiments was delivered using a self-contained Co-60 Foss Therapy irradiator at DCF. The irradiator delivered a maximum dose rate of 350 Gy min^{-1}, recorded at the time of running the experiment. However, the Hastelloy autoclave attenuates the majority of the gamma rays. Therefore, inserting three Co-60 pencils recorded a dose rate of approximately 37 Gy min^{-1} inside the autoclave. Dosimetry was carried out using solid state Harwell Amber dosimeters and Fricke dosimetry, as well as estimated through radiation shielding calculations.

During electrochemical measurements, the pre-transition or post-transition Zr-4 (or Zr-2.5Nb) samples act as a working electrode (WE), and platinum flags spot welded to platinum wire were used as both the reference (RE) and counter (CE) electrodes. The electrodes were sheathed with PEEK which also acted as a seal. A platinum reference electrode was used for the experiments as this was expected to be stable at both high temperatures and under irradiation, and could be used under reducing conditions. All electrochemical measurements were carried out using a Gamry 600+ potentiostat. The Open Circuit Potential (OCP) was measured for 3600 seconds prior to gamma irradiation to provide a baseline measurement (OCPgamma off). OCP measurements were then measured every 5 hours with gamma irradiation (OCPgamma on). To interpret the effect of gamma dose on electrochemical changes within the

oxide, the data was interpreted as a gamma irradiated Photo-Voltage (PV) signal. The PV records the difference between the OCP signal when the samples are being gamma irradiated compared to when there is no gamma flux (OCPgamma on − OCPgamma off). Therefore, a negative PV represents increased conductivity measured within the oxide, indicative of the generation of excess electrons within an n-type semiconductor under gamma illumination, whereas a positive PV shows the oxide behaving as if an anodic potential is being applied, suggesting an enhanced separation of electron-hole pairs and indicative of oxide dissolution [3].

3. Results

The accumulation of gamma dose has a clear effect on the PV response of both the pre-transition and post-transition Zr-4 oxides, as shown in Figure 1 at a temperature of 150 ºC. This effect is expected to be fundamentally related to generation of gamma photon generated charge carriers.
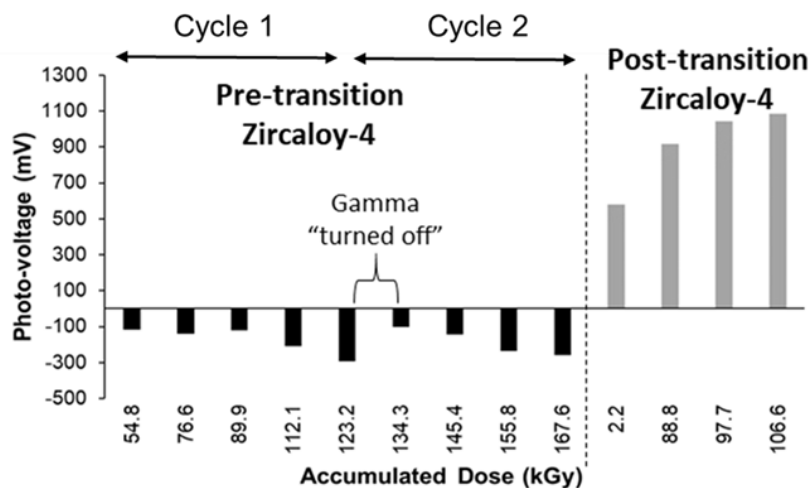

Figure 1: Photo-voltage response of Zircaloy-4 pre-transition (left) and post-transition (right) oxide with different accumulated gamma dose at 150°C.

Two cycles (cycle 1 and cycle 2) were carried out on the pre-transition Zr-4 sample, with the gamma flux turned off overnight for a period of approximately 15 hours. The results in Figure 1 show a relationship between decreasing (negative) PV with increasing gamma dose during cycle 1. This relationship shows enhanced electrical conductivity in the pre-transition oxide under gamma irradiation. Importantly, the results also show that the OCP of the working electrode after the overnight gamma-off period, before the start of cycle 2, approaches the original starting OCP measurement, recorded before the start of cycle 1. This drop in the OCP records electron-hole recombination and confirms n-type semiconductor behaviour. After the gamma flux was turned back on, the PV observed during cycle 2 then tracked in a very similar manner to the first cycle. The post-transition oxide behaves in an opposite manner, exhibiting a clear trend of increasing (positive) PV with increasing gamma dose. An increasing anodic PV is related to an increasingly oxidising environment within the thicker, post-transition, oxide structure, which develops under exposure to gamma photon irradiation. This increase in oxidising environment within the oxide could lead to enhanced dissociation of water, and thus an increase in radiolytic species, with increasing dose over time.
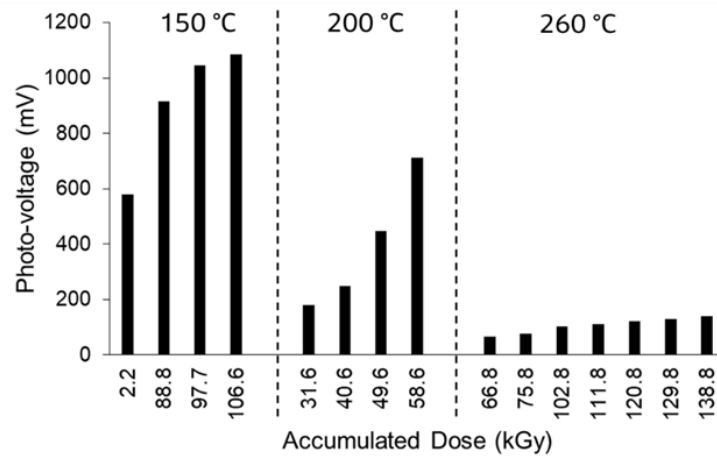
Figure 2: Photo-voltage response of Zircaloy-4 post-transition oxide with different accumulated gamma dose at different temperatures (150, 200 and 260 ℃).

Increasing the temperature from 150 ℃ to 260 ℃ steadily reduces the magnitude of the observed PV effect of gamma dose in the post-transition oxide sample, as shown in Figure 2. This confirms that temperature reduces the effect of gamma flux, on any developing oxidising environment within the oxide layer, reducing the measured anodic potential. Such an effect is thought to be related to the increase in temperature allowing any defects (electrons and holes), and radicals, generated by gamma radiation, to recombine more rapidly due to enhanced diffusion rates. This is supported by previous in-reactor observations that show an increased irradiation-induced corrosion enhancement at lower temperatures [4].

The PV signal for Zr-2.5Nb post-transition oxide at 150 ℃ showed a slightly increasing oxidising/anodic potential with accumulated gamma dose, as seen in Figure 3. Nevertheless, the magnitude of the changes in Zr-2.5Nb were far less than was observed in Zircaloy-4. Therefore, it can be postulated that the addition of Nb significantly reduces the oxidising/anodic potential of the post-transition oxide.
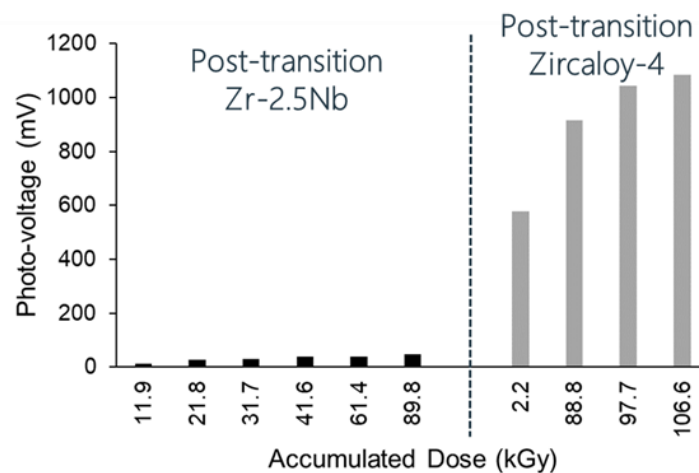

Figure 3: Photo-voltage response from post-transition Zr-2.5Nb at 150 ℃ compared to post-transition Zircaloy-4.

4. Discussion

The PV signals in both pre-transition and post-transition oxides can be understood in terms of the interaction of gamma radiation with the specific semiconductor properties of the barrier ZrO_2. Because ZrO_2 is a wide-gap n-type semiconductor, absorption of a photon (gamma ray) can produce electron-hole pairs (excitons), by ejecting electrons from a valence band into a conduction band. This effect results in enhanced oxide electrical conductivity [4]. Therefore, the observed negative PV change under gamma radiation of the pre-transition oxide in Figure 1 is believed to originate from an electric field induced by the photon-generated charge-carriers (i.e. holes and electrons). This relationship between gamma dose

and PV signal was further confirmed by repeating the irradiation cycle after turning the gamma flux off. When the gamma flux is turned off, the gamma-generated electrons and holes are able to recombine, which is indicated by an increase in PV back to its non-irradiated state. Then, as the gamma dose is turned back on, the negative PV signal strengthens with reproduction of the charge-carriers.

In the post-transition oxide, the large magnitude and positive nature of the PV signal records the environment becoming more oxidising with increasing gamma dose [4]. Although the stability of many oxidising species generated by gamma radiation are unclear, the bulk water was under an applied hydrogen overpressure, thereby limiting the lifetime of radiolytic species in the bulk water. A hydrogen overpressure is also used in PWRs to ensure a reducing environment is present. Nevertheless, radiolysis of water at the surface of a ZrO_2 powder interface has been shown to increase H_2 production, by Petrik et al., where it was also highlighted that the oxide band gap of ~ 5 eV corresponds to the energy required to break the H-OH bond within the water molecule [7]. Oxidising micro-environments also appear to occur within thick oxide films, as shown by Johnson [10], although a mechanism was not pinpointed at the time. Therefore, in this study, it seems that radiolytic oxidising species, such as OH and OH-, are being generated via a process of heterogeneous radiolysis in the pores of the thick oxide film, through the energy transfer of excitons to the water, which increase the measured PV. Ultraviolet (UV) radiation can also generate the same effect, as shown by Cox and Fidleris, who irradiated photoconductive ZrO_2 film with UV and found increased porosity and dissolution of the oxide barrier layer [11], although the penetration depth is severely limited in comparison to gamma.

Despite the potential for gamma radiation to significantly enhance the dissolution of ZrO_2, there has been little experimental investigation into the mechanism, providing some supportive evidence in corrosion films. The effect of an oxide interface on the radiolytic decomposition of water has been analysed by Petrik et al. [7], by comparing hydrogen yields (G-values) from adsorbed water on ZrO_2 powder with homogenous water vapour. Under gamma irradiation, the G-values were found to be significantly enhanced for water adsorbed on ZrO_2, which indicates that a process of heterogeneous radiolysis, via an effect of larger hole concentrations, appears to be linked to increases in the rate of water decomposition [7]. Petrik et al. also found that niobium (Nb) doping of Zr suppressed this water radiolysis effect [7]. The work presented here supports the observations by Petrik et al., showing the gamma radiation has a bigger impact on the oxide conductivity in post-transition oxides and we also observed that the Nb containing Zr alloy was far less affected by the gamma radiation in comparison to Zircaloy-4. Further work is also being done to analyse post-transition oxide images, using our in-house Zirconium Oxide Analysis Programme (ZOAP) to see if they contain a higher crack density following gamma irradiation.

Most empirical models that describe the corrosion rate are correlated to fast neutron flux only [12]. Although there are sound mechanistic justifications for correlating to neutrons, it is not the only radiation type that could affect corrosion processes. As demonstrated from this study, gamma radiation can also have a significant effect on the electrochemical processes that might enhance the corrosion kinetics. Excluding the effect of gamma radiation can lead to an under-prediction of Zr corrosion rates, as was found by Rishel et al., in regions of an ATR where the gamma to neutron flux is high [5]. In-reactor the gamma flux, temperature, and neutron flux, will all influence the oxidising environment within the oxide layer. In PWR conditions, the bulk coolant water is under a hydrogen overpressure, which limits the lifetime of oxidising species, meaning any effect of gamma radiation on pre-transition oxide is only ever very small. Nevertheless, post-transition, heterogeneous radiolysis leads to dissociation of water molecules on the internal surfaces of ZrO_2, where the porous water-permeated oxide meets the barrier oxide, and leads to local oxidising environments, impacting the protective nature of the barrier oxide layer, and leading to accelerated post-transition corrosion rates. Therefore, the incorporation of a gamma parameter is required in the empirical models to develop more accurate corrosion predictions and to reduce any conservatism in assessments for extending the lifetime of fuel elements.

5. Conclusion

To explore the dependence of zirconium alloy corrosion on gamma-only radiation dose electrochemistry tests on Zircaloy-4 and Zr-2.5Nb electrodes were performed using a mini-autoclave with PWR chemistry situated in a Co-60 gamma irradiator. The main points of this study are summarised.

- In the post-transition Zircaloy-4 samples increasing oxide dissolution with gamma dose was recorded as a large positive/anodic PV signal. This observation supports the hypothesis that gamma radiation causes the production of greater radiolytic oxidising species, generated via energy transfer of photon-generated holes within the porous fossil oxide film.
- Higher temperatures (200 and 260 °C) lead to a reduction in the measured oxidising/anodic potential caused by gamma irradiation, which is postulated to be a result of increased rates of diffusion and charge carrier recombination.
- The magnitude of the anodic potential with gamma dose was much smaller in the post-transition oxide film of Zr-2.5Nb, suggesting Nb additions suppress the mechanism of heterogeneous radiolysis, by acting as recombination sites within the oxide that shorten the lifetime and migration distance of charge carriers.

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