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The effect of Sn on corrosion mechanisms in advanced Zr-cladding for pressurised water reactors

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Abstract

The desire to improve the corrosion resistance of Zr cladding material to allow high burnup has resulted in a general trend among fuel manufacturers to develop alloys with reduced levels of Sn. While the detrimental effect of Sn on high temperature aqueous corrosion performance is widely accepted, the reason for it remains unclear. High-Energy synchrotron X-ray diffraction was used to characterise the oxides formed by autoclave exposure on Zr-Sn-Nb alloys with tin concentrations ranging from 0.01 to 0.92 wt.%. The alloys studied included the commercial alloy ZIRLO^{®1} and two variants of ZIRLO with significantly lower tin levels, referred to here as A-0.6Sn and A-0.0Sn. The nature of the oxide grown on tube samples from each alloy during autoclave testing at 360°C was investigated by cross-sectional Scanning and Transmission Electron Microscopy (SEM & TEM). Non-destructive synchrotron X-ray diffraction analysis on the oxides revealed that the monoclinic and tetragonal oxide phases display highly compressive in-plane residual stresses with the magnitudes dependent on both phase and alloy. Additional in situ Synchrotron X-ray diffraction experiments during oxidation at 550°C provided further confirmation of the

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trends seen for autoclave tested samples and demonstrated the presence of elevated levels of tetragonal phase in the initial stages of oxidation.

In situ and ex-situ measurements demonstrate unambiguously that the amount of tetragonal phase present and, more importantly, the degree of transformation from tetragonal to monoclinic oxide both decrease with decreasing tin levels, suggesting that tin stabilises the tetragonal phase. It is proposed that in Zr-Nb-Sn alloys with low Sn, the tetragonal phase is mainly stabilised by very small grain size and therefore remains stable throughout the corrosion process. By contrast, in alloys with higher tin levels larger, stress stabilised, tetragonal grains can form initially, but then transform as the corrosion front progresses inwards and stresses in the existing oxide relax.

Introduction

The importance of zirconium alloys in Pressurised Water Reactors (PWRs) is due to their low neutron cross-section, high corrosion resistance and sufficient mechanical performance during reactor service. During the initial stage of corrosion in high temperature pressurised water, zirconium alloys deviate from the expected parabolic rate law with a tendency towards cubic growth kinetics [1-5]. In general, once the oxide has grown to a few microns (pre-transition), a brief acceleration of corrosion kinetics is observed (post-transition), followed by a second cycle of parabolic/cubic growth rates. These cycles are repeated until accelerated linear corrosion occurs (breakaway) [3, 6-16]. Knowledge of these corrosion kinetics, and especially a more mechanistic understanding of transition and breakaway, is of great importance for undertaking accurate lifetime predictions for cladding tubes. During the gradual oxidation a large compressive stress is expected to build up inside the oxide due

to a Pilling-Bedworth ratio of 1.56 for the formation of zirconia from zirconium [1, 17]. This stress is believed to help stabilise the metastable tetragonal ZrO_2 [7, 18-20], and has been reported to form and accumulate near the oxide/metal interface [16, 19, 21, 22]. Compressive stress in the oxide must be balanced by tensile stress in the metal substrate and it has been argued that this will result in creep of the metal substrate with prolonged corrosion [19, 23], relaxing the compressive stresses in the oxide and generating a stress gradient with the highest stresses near the oxide/metal interface [19, 24]. As a result of this stress relaxation over time, the tetragonal ZrO_2 grains can become destabilised, resulting in a martensitic phase transformation to monoclinic ZrO_2 associated with a 5% volume expansion [25]. It has been suggested that this phase transformation results in the formation of cracks [26], which will eventually lead to breakdown of the barrier properties of the inner oxide acting. However, experimental evidence for a direct link between the tetragonal to monoclinic phase transformation and crack formation remains inconclusive. Other proposed factors that may contribute to stabilisation of the tetragonal phase include the effect of small oxide grain size (smaller than 25-30nm) [27-30] and defects induced by doping, but the concentration of dopants in the oxide is generally considered to be too low to play any significant role.

Tin is a common addition in the zirconium alloys widely used as fuel cladding material in light water reactors, and was originally introduced as an alloying element countering the poor corrosion resistance caused by nitrogen [31]. In PWR reactors, it is well known to have both positive and negative impacts on the in-reactor corrosion rate and growth acceleration at high burnups. A reduction of the tin content generally improves the corrosion resistance, e.g. for Zircaloy-4 [31] and advanced alloys like Westinghouse ZIRLO[®] [32, 33]. This insight

has been utilized over the years to improve cladding alloys by reducing tin content. However, tin is also known to provide a robustness and predictability of the corrosion behaviour, e.g. it protects against enhanced corrosion in high lithium and abnormal chemistry conditions [34]. Tin additions also reduce the corrosion enhancement around welds, and reduce the effect of irradiation on accelerating oxidation of zirconium alloys at high burnups believed to be due to hydrogen [35]. These contradictory effects of tin have been balanced in the latest generation of advanced alloys, e.g., Westinghouse Optimized ZIRLO^{TM2}.

The relationship between tin content and the volume fraction of tetragonal phase in the oxide is considered to be of great importance in terms of understanding its effect on corrosion [27, 36, 37]. It has been reported that decreasing tin levels lead to the formation of a thicker tetragonal barrier layer at the oxide/metal interface improving corrosion performance [37]. However, other researchers have found that the decrease of tin actually reduces the tetragonal phase fraction in the oxide grown on Zr alloys [27, 36]. The latter findings are further supported by studies on the stabilisation of tetragonal phase in structural tetragonal zirconia by tin, although in this case the required tin levels are comparatively high due to the larger oxide grain size [38, 39]. In general, the observations reported in these studies were all based on a very limited number of samples and used laboratory X-ray diffraction rather than high flux synchrotron X-ray diffraction. Considering the extremely low intensity of the tetragonal reflections used in such studies, the uncertainty from those findings must have been very high. To date, mechanistic studies on the effect of tin on corrosion performance have only been carried out in more traditional Zr

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alloys that do not contain any Nb. However, Nb containing alloys such as ZIRLO and M5^{®3} have now widely replaced traditional Zircalloys in fuel assemblies for PWRs.

In the present study, three Zr-Nb-Sn alloys with different tin contents (ZIRLO, A-0.6Sn and A-0.0Sn) were corrosion tested in an autoclave operating in simulated primary water conditions [40]. Autoclave tested materials were examined after different exposure times by high-energy synchrotron X-ray diffraction to study the stress state and the tetragonal/monoclinic ZrO₂ ratio in the oxide. (Preliminary results from these measurements were presented in [41]). The oxide microstructures were characterised by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

Additionally, in situ synchrotron X-ray diffraction was carried out during oxidation of ZIRLO and A-0.0Sn samples in air at 550°C to provide information about the state of the oxide during the early stages of formation. This investigation also eliminated much of the uncertainty associated with the limited number of measurements at different oxidation times possible for autoclave tested samples, as well as the sample to sample variation arising from using different autoclave tested samples to represent different exposure times. In situ testing allowed a single position on a single sample to be tracked while continuously collecting diffraction data.

Experimental

Materials Preparation

The alloys investigated in this study were recrystallized ZIRLO and two low tin versions (A-0.6Sn & A-0.0Sn). Corrosion samples of 30 mm in length (9 mm outer diameter, 0.8mm

³ M5[®] is a registered trademark of Areva NP.

thickness) were cut from tubes provided by Westinghouse. For in situ oxidation, 2 mm strips were prepared from the alloys with highest and lowest tin content. Chemical compositions of the alloys were determined at the EDF Research and Development facility in Moret-Sur-Loing, France and can be found in Table 1. Prior to corrosion testing all samples were pickled at 60°C in a solution of 10 vol.% hydrofluoric acid, 45 vol.% nitric acid and 45 vol.% distilled water for 3 minutes to remove inorganic contamination from the fabrication process.

Autoclave Corrosion

In order to record oxidation weight gain as a function of autoclave exposure, as well as generating samples that have experienced different duration of corrosion, a set of 4 samples from each alloy were introduced into the autoclave every 20 days, providing a total of 60 samples, subsequent 100 day exposures then provided samples over a range of times. Corrosion experiments were conducted in static isothermal autoclaves operating at 360°C in simulated primary water chemistry (Li and B were added in the form of lithium hydroxide and boric acid, Li= 2 wt.ppm, B = 1000 wt.ppm), at a saturation pressure of around 18 MPa (360°C). Careful weighing of all samples at regular intervals allowed the pre-transition corrosion kinetics of each alloy to be determined, with approximately 20 day increments. The results of the autoclave tests are summarised in Table 2. The tests were performed consistent with the ASTM G2 standard and are discussed in detail elsewhere [40]. The corrosion experiments aimed to provide samples and weight gain data from the early stage of corrosion until after the first transition.

Oxide Microstructure Characterisation

For imaging of the oxide after corrosion testing, cross-sectional samples were prepared for SEM. In order to protect the oxide during sample preparation, a Ni coating was applied to

each sample before cutting. Cross-sectional specimens were ground and polished carefully following standard metallographic procedures and etched in a solution of 5 vol.% hydrofluoric acid, 45 vol.% nitric acid and 50 vol.% distilled water at room temperature. A carbon layer (~5 nm thick) was deposited on freshly etched sample surfaces using a Gatan Model 682 PECSTM precision etching & coating system. The carbon layer improved the surface conductivity, preventing the accumulation of electrostatic charge, thereby minimising image artefacts. Imaging of the cross sectional samples was performed using a Philips XL30 FEG-SEM.

Further characterisation was carried out on ZIRLO samples by transmission electron microscopy (TEM). Thin specimens were extracted from samples with a range of exposure times using an FEI FIB200 instrument (5–30 kV gallium incident beam with beam currents of 50– 5000 pA) to give electron-transparent areas approximately 10 x 5 μm containing the whole oxide scale and some metal substrate. Samples were carefully thinned to provide a uniform thickness of <100 nm, to avoid the complex images that result with specimens much thicker than the oxide grain size. TEM characterization was carried out using a Philips CM20 microscope operated at 200 kV. Several TEM specimens were investigated from each sample to ensure the reproducibility of observations.

Synchrotron X-ray Diffraction

The advantage of using synchrotron X-rays over laboratory X-rays is the high flux and high peak position accuracy in conjunction with a low background, which enables the characterisation of minor phases such as the tetragonal phase in the present case. In this study, two types of diffraction experiments are discussed, in each case the penetration depth of the X-ray was such that measurements represented an average over the entire

oxide thickness. This was also demonstrated by the presence of strong diffraction signal from the Zr substrate for all measurements, as shown in the typical diffraction patterns in Figure 2.

Autoclave samples

Experiments to characterise the residual stresses in the oxide layer (monoclinic and tetragonal ZrO_2) the oxide layer and the metal substrate, together with the tetragonal/monoclinic phase fraction, were carried out on the EDDI beam line at BESSY, Berlin, an energy dispersive instrument dedicated to material science. A detailed description of the EDDI beam line has been given by Ch. Genzel et al. [42], and the general layout is shown in Figure 1a. Where the angle χ determined the component of in-plane stress measured, and $\psi=0$ to ensure that when $\varphi=0$ the crystal planes parallel to the specimen surface were sampled. The residual stress measurements were undertaken using the classical $\sin^2\psi$ approach [43] assuming a biaxial stress state in a Cartesian coordinate system. The elastic properties used for each phase are shown in Table 2 [24, 44]. Based on single crystal values of the monoclinic zirconia phase, E. Polatidis et al. [24] calculated polycrystalline diffraction elastic constants using an Elasto-Plastic Self-Consistent (EPSC) model [45]. EPSC modelling simulates deformation of polycrystalline aggregates by predicating the response of each grain within an infinite medium to predict the overall response of a given diffraction plane within the polycrystalline material. Due to the lack of reliable elastic properties for the tetragonal phase at room temperature (yttrium stabilised zirconia data was considered inappropriate), the current study applied the same monoclinic elastic constants to calculations regarding the tetragonal phase.

Since all measured samples had layers of oxide that were only a few microns thick, it is reasonable to assume that the out of plane stress in the oxide is zero. This assumption, in combination with the $\sin^2\psi$ technique, eliminates the need for a stress-free lattice parameter. Measurements were carried out with an incident beam and the EDX detector placed at 3° (i.e. $2\theta=6^\circ$) to the surface when the sample was at $\psi = 0^\circ$. Twenty one individual ψ angles ranging from 22° to 66° were selected based on the intensity of the spectrum at each angle, Figure 2a. This range corresponds to a $\sin^2\psi$ range of 0.14 to 0.84. All stress data presented here are representative of the hoop direction of the cladding tube. Initial measurements carried out in the both axial and hoop directions showed no significant differences between the stresses in the two directions. A BESSY II in-house analysis program written in MATHEMATICATM was used for processing the output files. It applies pseudo-Voigt peak fitting for a selected energy range and produces plots of $\sin^2\psi$, peak intensity, peak position and widths at half maximum of each peak (FWHM). In general, accurate peak analysis of the diffraction signal from a thin monoclinic/tetragonal oxide layer is inherently difficult due to many overlapping peaks and the nano-sized grain structure resulting in peaks that are both low in intensity and broad. In the present case, the reflections from the oxide that could be fitted with the highest certainty were the $(\bar{1}11)$ reflection of the monoclinic phase and the (101) of the tetragonal phase. In addition, the $(10\bar{1}1)$ reflection of the α -zirconium phase and (111) reflection of the monoclinic phase were also analysed. A typical diffraction spectrum of autoclave tested material can be seen in Figure 2, highlighting the limited quality of the tetragonal ZrO_2 (101) reflection. Note that hydrogen generated during prolonged autoclave testing led to the formation of hydrides when the material was cooled to room temperature. This resulted in the observation of a weak (111) reflection of the δ Zr-hydride phase. In order to minimise texture effects in the

oxide when determining the integrated intensity (I) of each phase, the data were averaged along the range of ψ angles. A more detailed description of the data analysis carried out during such studies can be found in [24].

In situ oxidation

To provide a higher density of measurements as a function of oxide growth, and thereby increased confidence in the trends observed in autoclave tested samples, synchrotron XRD measurements were performed whilst samples were exposed to air at 550°C. This temperature was chosen in order to maximise oxide growth in the beamtime available. To achieve in situ oxidation, an electro-thermal mechanical tester (ETMT) was mounted onto a large sample stage at the I12 beamline, Diamond light Source. Resistive heating in the ETMT ensured excellent temperature control of samples while still allowing easy access for the X-rays onto the oxides as they formed. A schematic of the set-up is shown in Figure 1. Diffraction measurements were carried out directly opposite to the position where thermocouples were spot welded to the samples, ensuring careful control of the oxidation temperature in the region of interest. Diffraction patterns produced by the sample from a monochromatic incident beam (79 keV), were recorded every five seconds using a high resolution 2D detector (Thales Pixium RF4343) as the sample was heated in air. Figure 2 shows a typical diffraction pattern obtained after only 4s exposure time, when the oxide peaks became visible. To improve the peak intensities for fitting, images were summed together in sets of 20, resulting in a final time resolution of 100s for the data presented here. Once summed, images were integrated circumferentially to provide diffraction profiles at every five degrees relative to the sample surface. From the resulting profiles, pseudo-Voigt peak fitting was applied to the monoclinic ($\bar{1}11$)/(111) and tetragonal (101) peaks using

MatlabTM scripts. This procedure provided time-resolved peak intensity and position for each peak as a function of angle to the sample surface. By applying the $\sin^2\psi$ technique, as discussed earlier, it was possible to evaluate the average stress in the two oxide phases as a function of time. The relative intensities of the tetragonal and monoclinic peaks were used to calculate the evolution of tetragonal phase fraction.

It should be noted that it was not possible to measure the weight gain of the in situ oxidised samples, so only the oxidation time can be plotted for these experiments. Further controlled exposures are planned in the future to correlate oxidation time to the thickness of oxide produced, thereby allowing the evolution of stress and tetragonal phase to be related directly to oxide thickness.

Results

Autoclave Corrosion

The corrosion kinetics of autoclave tested ZIRLO, A-0.6Sn and A-0.0Sn samples are presented in Figure 3 as corrosion weight gain against autoclave exposure time. Note that instead of presenting averaged values for each group of notionally identical samples, data for each individual sample are plotted in Figure 3, illustrating the level of scatter observed during the experiment.

The tested materials exhibited typical corrosion performance with an indication of a change from pre- to post-transition kinetics at around 140 days in the case of ZIRLO and 140-240 days in the case of A-0.6Sn. Before transition, the oxide appeared black in all samples. During transition, specimens exhibited patches where the oxide had become grey in colour. Note that in the case of A-0.6Sn, a very long transition phase of about 100 days was

detected. Interestingly, corrosion tests carried out on material with identical chemistry, but in a partially recrystallized condition, did not show such a long transition phase [40].

With up to 260 days of autoclave exposure, A-0.0Sn showed no sign of a transition in oxidation kinetics. A universally black oxide was observed on pre-transition samples as early as after 20 days and as late as after 260 days of corrosion testing. A second series of autoclave exposures aimed at recording long term corrosion kinetics also confirmed that A-0.0Sn showed no sign of transition up to 360 days of exposure (i.e. $\sim 45 \text{ mg/dm}^2$ weight gain). However, after 540 days of exposure, the oxides appeared to be post-transition in nature due to the presence of clearly delineated dark and light patches on their surfaces and $\sim 80 \text{ mg/dm}^2$ weight gain.

Oxide Microstructure

SEM analysis showed that in the early stages of corrosion (10 days of exposure), a continuous oxide layer ($\approx 1 \mu\text{m}$) with almost no visible cracks and a smooth oxide/metal interface was present for all three alloys, Figure 4(a), (c) and (e). The oxide thickness, measured by using the FEG-SEM images, was consistent with that calculated from oxidation weight gain ($15 \text{ mg/dm}^2 = 1 \mu\text{m}$ [46, 47]).

Figure 4(b), (d) and (f) show cross-sectional FEG-SEM images taken when each alloy had gained about 30 mg/dm^2 weight. This corresponded to an exposure time in the autoclave exceeding 120 days in the case of ZIRLO samples, 160 days in the case of A-0.6Sn and 180 days in the case of A-0.0Sn. In the case of ZIRLO and A-0.6Sn, the examined samples were near to the exposure time where transition occurred. It can be seen that at this stage the oxide had developed some short and medium sized cracks. In A-0.0Sn alloy, where the

examined sample was still more than 180 days prior to the 1st transition, the oxide displayed only very few small cracks.

A more detailed illustration of the pre-transition oxide microstructure found in the ZIRLO samples is provided by the TEM bright field images in Figure 5 & Figure 6. The oxide thicknesses observed by TEM show good agreement with those from SEM and weight gain measurements. The images display the typical columnar oxide grain structure often reported for zirconium alloys over most of the oxide. The columnar grains were always observed to grow roughly perpendicular to the metal-oxide interface, with an average grain size of about 14-40 nm x 135-230 nm, occasionally interrupted by smaller equiaxed grains 10-30 nm in diameter (Figure 6b). Additionally, a region approximately 200nm thick was observed at the outermost part of all the samples studied (i.e. the first oxide to form) consisting almost entirely of equiaxed grains and usually associated with extensive porosity (Figure 6a).

Ex-situ Residual Stress and Phase Fraction Analysis

A number of autoclave tested specimens were investigated using synchrotron X-ray diffraction as described above and in [24, 48]. Specimens were selected from relatively early stage of corrosion, i.e. before and shortly after the 1st transition. Since samples at transition display a patchy surface of grey (post transition) and black (pre transition) oxides, measurements were carried out in both areas. Measurements of the residual stresses in the metal substrate consistently showed tensile stresses of up to +150 MPa. In Figure 7 the measured oxide stresses (monoclinic and tetragonal phase) are plotted as a function of corrosion weight gain for ZIRLO, A-0.6Sn and A-0.0Sn. In both ZIRLO and A-0.6Sn the oxide stresses in the monoclinic phase were about -700 MPa to -1000 MPa regardless of the

corrosion weight gain, while stresses in A-0.0Sn samples were slightly lower in magnitude (-500 to -900 MPa) and accompanied by greater scatter. It should be noted that while detailed comparisons of the oxide texture are not given here, the diffraction patterns from different oxides showed no significant differences in terms of their crystallographic texture.

The stresses measured in the tetragonal oxide phase had considerably higher uncertainty than the stresses measured in the monoclinic phase due to a very weak tetragonal (101) reflection, see Figure 2. The stresses determined in the tetragonal phase were generally between -1300 to -2100 MPa for ZIRLO and A-0.6Sn samples. It can be seen from Figure 7(f) that A-0.0Sn displayed very large stress variations in the tetragonal phase, with compressive stresses as low as -500 MPa and as high as -2400 MPa.

Figure 8 shows the calculated tetragonal phase fraction and the equivalent layer thickness of the tetragonal phase as a function of weight gain. The calculation is based on the Garvie-Nicholson equation [49]:

$$\text{Tetragonal Fraction} = I_{tet(101)} / [I_{tet(101)} + I_{mono(111)} + I_{mono(\bar{1}11)}].$$

However, in this case, the Garvie-Nicholson equation was modified to include the integrated intensity of I averaged over all the ψ angles, thereby reducing the influence of any crystallographic texture present in the tetragonal phase. An equivalent layer thickness of the tetragonal phase was calculated by normalising the calculated tetragonal phase fraction with the measured corrosion weight gain. In contrast to the calculated tetragonal fraction, the theoretical equivalent tetragonal phase thickness aims to take the oxide thickness into consideration. Figure 9 shows schematically, in a simplified manner, the expected distribution of tetragonal and monoclinic ZrO_2 based on observations such as [16, 19]. It

highlights that with continuous growth of the oxide the ratio of tetragonal/monoclinic phase is expected to decrease, although the absolute volume of tetragonal oxide might remain unchanged. Such a trend is indeed observed in our new data, particularly for ZIRLO and to a slightly lesser degree for A-0.6Sn, Figure 8 (a) and (b), although during the early stages of corrosion the tetragonal phase fraction is significantly lower in A-0.6Sn compared to ZIRLO. In contrast, A-0.0Sn shows hardly any change of the tetragonal/monoclinic ratio with increasing weight gain and a very low tetragonal phase fraction from the first measurement point, i.e. after only 10 days of corrosion. The present results, based on a large number of samples, clearly show that tin increases the tetragonal phase fraction in agreement with observations by [27, 36], but contradicts the observations of [37]. Finally, a decrease of the tetragonal phase fraction from pre- to post- transition conditions was observed in A-0.6Sn and A-0.0Sn.

In situ Residual Stress and Phase Fraction Analysis

The evolution of tetragonal phase fraction for ZIRLO and A-0.0Sn during oxidation in air at 550°C is shown in Figure 10. These results confirm the observations made for ex-situ measurements, where a reduced fraction of the tetragonal phase was seen for the lower tin alloys. As with the measurements on autoclave samples, the tetragonal phase fraction for the oxides grown on ZIRLO is about twice that present in the low tin alloy (A-0.0Sn). However for oxidation at 550°C in air, the tetragonal phase fractions were significantly higher than found in the autoclave samples, with average fractions of around 30% and 15% for ZIRLO and A-0.0Sn respectively after 14 hours exposure. In addition to the data after prolonged oxidation, the in situ experiment was also able to track the evolution of the tetragonal phase in the very early stages of oxidation, providing information not available

from previous ex-situ measurements. This early corrosion data shows that initially the oxides formed on both alloys contain very high fractions of the tetragonal phase. For ZIRLO the tetragonal phase makes up around 65% of the initial oxide formed, while for A-0.0Sn the initial tetragonal fraction is as high as 40%. This high initial tetragonal content appears to correlate with TEM images from the upper (first formed) oxide, that show a high concentration of equiaxed grains. In both cases the tetragonal fraction drops rapidly in the first 2 hours of oxidation and for A-0.0Sn the tetragonal fraction appears to plateau after around 6 hours. The tetragonal fraction for ZIRLO, however, seems to continue to gradually fall for the duration of the experiment, resulting in a difference of only about 5% between the two alloys after 14 hours of oxidation.

Figure 11 illustrates the evolution of the in-plane residual stresses present in the monoclinic oxide for the two alloys. In contrast to the results shown in Figure 7a for the autoclave tested samples, a clear difference is seen between the two alloys when oxidised at 550°C in air. For ZIRLO these compressive stresses are fairly constant at 1300-1400MPa over the entire 14 hr exposure time. However, for the A-0.0Sn alloy the monoclinic stresses are significantly lower and relax significantly over the as oxidation proceeds, from around 900MPa initially to about 600MPa after 14 hrs exposure.

For the stresses measured in the tetragonal phase for the two alloys, Figure 12, the trend is more similar to that seen for autoclave tested samples, with significantly lower compressive stresses for A-0.0Sn (0-1500MPa) than for ZIRLO (1500-3500MPa). As with the ex-situ measurements, the relatively low intensity of the tetragonal peak results in a high degree of scatter. However, the large number of data points recorded demonstrates that there is a clear difference between the stress state of the tetragonal phase formed on these two

alloys. Both alloys appear to show a gradual relaxation of the compressive stresses in the tetragonal phase over the course of the experiment.

Discussion

It should be noted that varying the tin content of an alloy does not necessarily result in a change in the tin level of the resulting oxide. However, recent 3-D atom probe analysis has confirmed that during corrosion of Zr alloys, the tin/zirconium ratio is similar in the metal and oxide (i.e. tin present in the metal passes into the oxide without partitioning as corrosion progresses) [48, 50]. This is a very important observation as it shows that differences in tin levels between alloys will be carried over into the oxide, where they can have an influence on the relative stabilities of the oxide phases.

Tin content and corrosion

The improved resistance to aqueous corrosion achieved in Zr alloys by reducing the tin content has been previously demonstrated for Zircaloy-4 [31] and advanced alloys like Westinghouse ZIRLO [32, 33]. The corrosion kinetics recorded for the three Zr-Nb-Sn alloys discussed here also confirm this trend [40]. Despite very similar pre-transition corrosion kinetics, a significant delay in the onset of transition was observed with reduced tin content. The ZIRLO showing signs of transition (defined by the acceleration of corrosion kinetics and the appearance of grey patches on the oxide surface) after only 140 days, while for the lowest tin alloy (A-0.0Sn) transition was only reached after more than 360 days.

It should be noted that despite these apparent benefits of reducing tin levels, it is also well known that the addition of tin is advantageous for in-reactor performance, providing robustness and predictability of the corrosion behaviour in high lithium and abnormal

chemistry conditions [34]. A better understanding of the mechanism by which tin affects corrosion, would allow these competing factors to be more effectively balanced.

The importance of tetragonal phase fraction

Understanding the structure of the oxide that forms on Zr alloys is vital to determining the processes that control the inward diffusion of oxygen ions across the oxide film and thereby define the pre-transition corrosion kinetics [12]. It remains unclear whether diffusion of oxygen along crystallite boundaries or bulk diffusion through a perfect oxide are the dominant factors [51]. However, it is generally accepted that the relationship between the two oxide phases may play an important role. The tetragonal phase has often been reported to accumulate near the oxidation progression front, the oxide/metal interface. This observation has often led to suggestions that the tetragonal phase acts as a barrier layer for oxygen diffusion [10, 16, 19, 21, 22, 52]. Consequently, the improved corrosion resistance observed with reduced tin content for a range of Zircaloy-4 type alloys was attributed by K. Takeda and H. Anada [37] to a degradation of the tetragonal phase. Their laboratory based X-ray measurements, however, suggested that the tetragonal phase fraction increases as the tin content is reduced. According to the degradation model put forward, the tetragonal to monoclinic phase transformation is accelerated by oxidation of the tin segregated within the oxide, resulting in increased porosity. However, combining the facts that (i) the tetragonal phase fraction was only determined for a single sample in each alloy (and considering the experimental uncertainty when measuring the volume fraction of this phase by laboratory x-ray diffraction), (ii) that in the very large number of published TEM studies of oxides on Sn-containing zirconium alloys no unambiguous identification of tin oxide

phases has been reported, and (iii) the general observation that tin does in fact stabilise the tetragonal phase, it seems unlikely that this model is correct. One of the key findings of the current work has been that the tetragonal/monoclinic ratio is strongly depending on the thickness of the oxide, which demonstrates that comparisons between the tetragonal phase fractions of different alloys are only meaningful when multiple measurements are conducted as a function of corrosion weight gain.

Evaluating tetragonal phase fraction

Evaluating differences in the evolution of tetragonal phase fraction between different alloys can be challenging even when comparing trends for multiple measurements over a range of corrosion weight gains. For the measurement technique used here, the tetragonal fraction obtained represents an average over the entire oxide, so from a single measurement it is impossible to distinguish between tetragonal phase that is evenly distributed over the entire oxide and that which may be concentrated near the metal oxide interface. The schematic shown in Figure 9 illustrates three possible scenarios for the distribution of tetragonal phase as the oxide layer grows, along with the evolution of tetragonal phase fraction that might be observed for each. The schematic demonstrates that when the tetragonal phase is evenly distributed throughout the oxide, a constant fraction would be measured regardless of oxide thickness. Conversely, if most of the tetragonal phase was concentrated near the oxide/metal interface, as has been often suggested, the measured tetragonal fraction would fall with increasing oxide thickness, even though the total volume of tetragonal phase present may remain constant. It is important to consider these effects when evaluating measurements of tetragonal phase fraction.

Measurements on the autoclave tested samples show that the oxide formed on ZIRLO contains in the early stages of oxidation the highest tetragonal phase fraction. This fraction falls significantly as corrosion proceeds (Figure 8a), suggesting that the tetragonal phase is not uniformly distributed over the oxide. This is further confirmed by the near horizontal trend calculated for equivalent tetragonal layer thickness shown in Figure 8b. Comparing the evolution of tetragonal phase fraction for the three alloys in Figure 8, it is evident that as the tin content is reduced the initial tetragonal/monoclinic ratio also decreases. Furthermore, the drop in tetragonal phase fraction with overall weight gain (i.e. the gradient in Figure 8) also reduces with decreasing tin. For the lowest tin alloy, A-0.0Sn, the tetragonal phase fraction appears to be nearly constant with weight gain, suggesting that for this alloy the tetragonal phase approaches a uniform distribution throughout the oxide. The data from in situ oxidation experiments (Figure 10) confirms the trends observed for autoclave tested samples, with the oxide formed on ZIRLO showing a much higher tetragonal phase fraction than that on A-0.0Sn. The latter stages of the experiment, i.e. after 6 hours oxidation, also suggest a continued gradual decrease in the tetragonal phase fraction for ZIRLO, while for A-0.0Sn a plateau seems to have been reached. However, it is in the initial stage of oxidation where the in situ experiment may be able to provide additional insight into the corrosion mechanisms. Very high initial tetragonal phase fractions were recorded, even for the low tin alloy, which reduced rapidly over the first 2 hours of oxidation. This observation would suggest high levels of phase transformation may be taking place in the early stages of oxidation. Importantly, even at this early stage of corrosion ZIRLO still showed significantly higher tetragonal phase fraction.

To understand this apparent variation in tetragonal phase distribution it is important to consider the mechanisms by which the tetragonal phase can be stabilised. The mechanism most commonly used to explain the stabilisation of tetragonal grains near the oxide/metal interface is that of high compressive stress [16, 24, 53-58]. This compressive stress is related to the volume increase when Zr transforms to ZrO_2 (Pilling-Bedworth ratio is 1.56) [57, 59]. However, this stress has been shown to relax in the oxide away from the oxide/metal interface as corrosion progresses [24], therefore its stabilising effect is limited to the oxide directly adjacent to the interface resulting in higher levels of tetragonal phase in this region.

If stress was the only factor affecting the stability of the tetragonal phase, it would be expected that as corrosion progresses, and the stresses in the existing oxide relax, all the tetragonal phase present would eventually transform to monoclinic oxide. However, there is sufficient experimental evidence from measurements on thick oxides [19], that even in regions with low stresses some tetragonal phase remains present. For these regions it is believed that the grains of the tetragonal phase are small enough to result in stabilisation without the need for an external compressive stress. In the case of a Nb-free Zr alloy it has been suggested that this critical grain size is about 30 nm [27], as can readily be observed in TEM images like that shown in Figure 6(a).

In the case of ZIRLO and A-0.6Sn, stresses measured in the tetragonal phase were generally between -1500 MPa and -2000 MPa, for both autoclave samples and in situ oxidation (Figure 7 & Figure 11). Stress measurements of the tetragonal phase in oxides on A-0.0Sn showed significantly more scatter, but generally the observed stresses were similar to those for the monoclinic phase, i.e. less compressive than the tetragonal stress values for the other alloys. This difference suggests that the majority of tetragonal phase in A-0.0Sn is not stabilised by

stress but by grain size. It should be noted that the high volume of data available from the in situ experiment is important as it provides additional confidence that this observation is valid despite the large scatter in the stress data for the tetragonal phase on A-0.0Sn.

The results suggest that in the presence of tin, tetragonal grains can be readily stress stabilised, but that when tin is below a critical level the stresses alone are not sufficient to stabilise grains that exceed a certain critical grain size. The high initial tetragonal phase fraction observed during in situ oxidation may be related to the combination of a highly stressed oxide with the high proportion of small equiaxed oxide grains present at this early stage of oxidation. The presence of a high proportion of small equiaxed grains early on in oxidation has been confirmed for the autoclave tested ZIRLO samples by the TEM images in Figure 5 & Figure 6.

Whilst the higher temperature air oxidation used for the in situ experiment may not provide the ideal comparison to the autoclave exposures, it is encouraging that despite some differences in absolute tetragonal fraction and stress levels, very similar trends are observed between different alloys for in situ and ex-situ oxidation. Further experiments are planned with oxidation to be carried out in situ at temperatures more similar to those used for autoclave testing and the possibility of in situ autoclave exposures is currently being investigated.

It should be noted that some differences are observed between the two experiments in terms of the monoclinic residual stresses measured for each alloy. For the lower temperature autoclave exposures, the monoclinic stresses are very similar for all three alloys. However, when oxidation was performed at 550°C in air, the stresses measured in the monoclinic phase the A-0.0%Sn oxide was significantly lower. This reduced stress may

be attributed to the significant difference in creep properties of the two alloys at this temperature, due to the reduction in the solid solution strengthening provided by tin. As the creep strength of the alloy decreases, the level of constraint is reduced and less compressive stress can be maintained in the oxide. However, the difference in residual stresses for the tetragonal phase between the two alloys appears to be independent of oxidation temperature, and is therefore not expected to be related to the mechanical properties of the alloys.

As discussed earlier, accurate elastic properties are not available for tetragonal zirconia at the temperatures studied here. For this reason, monoclinic elastic properties have been applied to both phases. This may introduce an added uncertainty with regard to the absolute magnitude of the stresses present in the tetragonal phase. However, since the current work is concerned with how the stress state changes over time for the oxide phases of each alloy and how this relates to the tetragonal phase fraction, the lack of precise elastic properties should not impact greatly on the findings presented.

Proposed model for transition

Based on the current observations and discussions, we propose an updated model to describe the oxidation of Zr-Nb-Sn alloys, illustrating one factor that contributes to the transition from slow to accelerated growth kinetics, Figure 13.

When ZrO_2 first nucleates at the metal surface a large proportion of new oxide grains may be tetragonal, stabilised by a combination of their small grain size, the large compressive stress present and by any tetragonal stabilising elements present in the alloy. Those grains that are suitably oriented will begin to grow epitaxially as corrosion proceeds. If these grains are tetragonal, and a tetragonal stabiliser such as tin is present, they may continue to grow

whilst under the influence of a compressive stress. These grains will, however transform, to monoclinic oxide if the compressive stress is relaxed over time. As a result, stress stabilised tetragonal grains will only maintain their crystal structure near the interface, resulting in a layer with high tetragonal/monoclinic fraction as shown in Figure 9b-c. Tetragonal grains that do not have the correct orientation will not grow, and may stay below a critical grain size that enables them to remain tetragonal in the absence of a compressive stress. These size stabilised tetragonal grains may therefore be uniformly distributed throughout an oxide. Oxides with higher levels of phase transformation may be subject to more extensive crack formation according to the shear model previously described by a number of researchers [3, 26, 60].

During the pre-transition phase of corrosion, the rate of oxide growth slows down over time, so the rate at which new, highly-stressed oxide forms also decreases. However, relaxation mechanisms may still be acting on the oxide. The combination of these factors would result in a gradual reduction in the thickness of the region where the oxide is highly-stressed and where the tetragonal phase will remain stable. Eventually, the damage in the oxide caused by phase transformation will occur close enough to the interface to produce a breakdown in the integrity of the oxide, initiating the observed transition in oxidation kinetics.

A critical aspect of this model is the distinction between grain size and stress stabilised tetragonal grains, and that the Zr alloy chemistry affects the volume fraction of tetragonal grains that can be stress stabilised and can transform once the stress has decreased. The epitaxial growth of tetragonal grains is rare in material with lower tin content, as transformation would occur as soon as the grain becomes enlarged. When the interface moves away from the previously formed oxide, stress stabilised tetragonal grains may still

transform into monoclinic oxide, but the total volume of material transforming would be much smaller than in material with higher tin content. The reduced amount of transformation brings about slower formation of a smaller volume of cracks (Figure 4 f), and subsequently a longer pre-transition period (Figure 3c). For the three alloys investigated in the present work, i.e. Nb containing Zr alloys, the proposed model seems to be responsible for the different time it takes for transition to occur. However, it remains to be confirmed that this model is also valid for other alloy systems.

It has not yet been possible to directly relate the level of tetragonal/monoclinic phase transformation to observations of oxide breakdown in the different alloys. Transmission electron microscopy studies (TEM) may be a possible way to attempt this, and observations on ZIRLO have already suggested the presence of nano-porosity at oxide grain boundaries which appears to become more linked up nearer to the interface as transition is approached [61, 62]. However, such investigations will only be able to evaluate the differences in how damage (i.e. porosity) evolves over time for different tin levels. It is not possible to accurately determine the presence of stress stabilised tetragonal grains by TEM since the preparation of the thin foil samples needed for TEM analysis would necessarily result in the relaxation of stresses in the oxide and thereby transformation of any such tetragonal grains. Other diffraction based studies have been able to successfully determine the distribution of the tetragonal phase within the oxide by studying cross-sectional samples [16, 63]. This technique only interrogates material near to the surface of cross-sectional specimen or through very thin cross-sections, and therefore may not always represent the stress state and phase distribution present in the bulk oxide, due to the effect of sample preparation on the constraint present. However, the results from these studies are in good agreement with

the model proposed here, as they suggest that oxides with higher levels of tetragonal phase near to the oxide/metal interface are likely to reach transition earlier. The current work reinforces these findings by comparing the evolution of tetragonal phase for each alloy over a range of exposure times.

It should also be noted that tin may also affect the transport of hydrogen in zirconium alloys during oxidation, thereby impacting the corrosion rate after extended exposure. Initial observations for samples cathodically charged to induce a hydride rim before corrosion testing, suggest that alloys with low tin levels may experience some outward depletion of their hydride rim through the oxide layer during corrosion [40]. Further tests to investigate this phenomenon are under way, tracking the movement of hydrogen during corrosion by performing NanoSIMS on selected specimen partially-corroded in isotopically spiked water.

Summary

The mechanisms of oxide formation on three recrystallized Zr-Sn-Nb alloys with different tin contents (ZIRLO®, A-0.6Sn and A-0.0Sn) have been investigated by performing aqueous corrosion at 360°C and 18 bar in simulated primary water and by in situ oxidation in air at 550°C. The results shed new light on the oxidation mechanism that leads to transition of the corrosion rate. The following observations have been made:

1. Corrosion resistance during autoclave exposure improves significantly with decreasing tin content.
2. Compressive stresses in the monoclinic oxide phase were within the range of -700 to -1000 MPa in the case of ZIRLO and A-0.6Sn, while for A-0.0Sn lower stresses of -500 to -900 MPa were measured. Compressive stresses in tetragonal phase were -1500

to -2000 MPa in both ZIRLO and A-0.6Sn. A-0.0Sn displayed stresses in the tetragonal phase similar to the stresses in the monoclinic phase.

3. Oxidation in air at 550°C produced slightly different stresses, but the trends between alloys remained the same. Monoclinic stresses were within the range of -1200 to -1500 MPa for ZIRLO and -600 to -1000 MPa for A-0.0Sn. While the tetragonal stresses were -1500 to -3000 MPa for ZIRLO and -1500 to 0 for A-0.0Sn.
4. Tetragonal phase fractions and equivalent layer thickness of the tetragonal phase were calculated for autoclave tested samples. It was possible to demonstrate that tin contributes to the stabilisation of the tetragonal phase. It was also inferred that the rate of tetragonal to monoclinic phase transformation reduces with decreasing tin content.
5. In situ synchrotron X-ray diffraction measurements during oxidation provided, for the first time, information about mechanisms at work during early oxidation. These measurements demonstrated that, regardless of tin content, elevated levels of tetragonal phase are present when oxidation first initiates, but that these levels are significantly higher for ZIRLO than for A-0.0Sn.
6. A model explaining the corrosion mechanisms leading to the rate transition phenomenon has been proposed highlighting the distinction between grain size stabilised and stress stabilised tetragonal grains. It assumes that stress stabilisation of tetragonal oxide phase is only possible in combination with some chemical stabilisation, which in the present case is by tin.
7. The model identifies the stress stabilised tetragonal phase as detrimental to the corrosion performance due to stress relaxation in the oxide enabling tetragonal to

monoclinic phase transformation with an associated shear strain and volume expansion.

8. The observation of stress-stabilised tetragonal phase is only possible via a bulk technique, where the material constraint is maintained. Therefore, the presence of such grains cannot be confirmed by TEM analysis.

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Figures and Tables

Table 1: Measured chemical composition of the materials.

Alloy	Alloying Elements				
	Zr	Fe[wt%]	Sn[wt%]	Nb[wt%]	Hydrogen [wt.ppm]
Recrystallised ZIRLO	balance	0.09	0.92	0.91	10
Recrystallised A-0.6Sn	balance	0.09	0.66	0.91	4
Recrystallised A-0.0Sn	balance	0.08	0.01	0.90	17

Table 2: Summary of autoclave corrosion results.

Alloy	Time to Transition	Max. t	Max. ΔW
	(days)	(days)	(mg/dm ²)
A-0.0Sn	> 360	540	78.7 ± 0.8
A-0.6Sn	140 - 240	260	56.2 ± 3.7
ZIRLO	140	160	43.2 ± 2.9

Table 3: Elastic constants used for stress calculation.

Phase		Young's Modulus	
		Poisson's ratio	(GPa)
ZrO ₂	[39, 41]	0.282	253
α-Zr	[40]	0.34	96

Figure 1: Schematic layout of a) the main beamline components at EDDI, BESSY II [42] and b) the in situ oxidation set-up used at I11, Diamond Light Source.

Figure 2: Diffraction results, showing a) a 2D plot intensity variation with tilt ψ angle, captured at BESSY II EDDI beamline, on the oxide of a ZIRLO sample at diffraction angle $2\theta=6^\circ$ and b) diffraction rings recorded for a ZIRLO sample during in situ oxidation at I12, Diamond Light Source.

Figure 3: Autoclave corrosion weight gain profile of recrystallized ZIRLO up to 180 days of autoclave exposure, and recrystallized A-0.6Sn and recrystallized A-0.0Sn up to 260 days. Note that measurements above 300 days were taken from a separate, long term autoclave, test running under similar conditions, but with fewer interruptions.

Figure 4: Back-scattered electron mode SEM images representative of the oxide (cross-section) (a) ZIRLO after 10 days of autoclave exposure, (b) ZIRLO (120 days exposure), (c) A-0.6Sn (10 days exposure), (d) A-0.6Sn (160 days exposure), (e) A-0.0Sn (10 days exposure) and (f) A-0.0Sn (180 days exposure). Note that an Au layer was deposited on top of the oxide prior to Ni-coating to improve the electrical conductivity of the surface for subsequent electroplating.

Figure 5: TEM bright field images showing morphology of oxides formed on ZIRLO after a) 34 days, b) 60 days c) 100 days of autoclave exposure.

Figure 6: TEM images of the oxide formed ZIRLO after 100 days of autoclave exposure, showing a) the high density of small equiaxed grains present at the outermost part of the oxide and b) the less commonly seen equiaxed grains occasionally interrupting the columnar grains further away from the outer oxide surface.

Figure 7: The evolution of hoop stresses in a) the monoclinic and b) tetragonal oxide phases formed on ZIRLO, A-0.6Sn and A-0.0Sn during autoclave exposure at 360C water.

Figure 8: Calculated a) phase fraction and b) equivalent layer thickness of tetragonal phase plotted as a function of weight gain measured on ZIRLO, A-0.6Sn and A-0.0Sn.

Figure 9: Schematic illustrating three possible distributions of tetragonal phase in the oxide during the inward corrosion of Zr, where the tetragonal phase is a) uniformly distributed, b) concentrated only near the oxide/metal interface and c) concentrated at the interface but also remains present further away (N.B. shaded region represents the presence of tetragonal phase). The evolution of the average tetragonal phase fraction that would be observed for each is shown, as well as the volume of tetragonal phase this represents.

Figure 10: The evolution of tetragonal phase fraction during the oxidation of ZIRLO and A-0.0%Sn at 550°C for 14 hours.

Figure 11: The evolution of residual stresses in the monoclinic phase of the oxides formed during the oxidation of ZIRLO and A-0.0%Sn at 550°C in air for 14 hours.

Figure 12: The evolution of residual stresses in the tetragonal phase of the oxides formed during the oxidation of ZIRLO and A-0.0%Sn at 550°C in air for 14 hours.

Figure 13: Schematic description of corrosion mechanisms in material with higher tin content and material with lower tin content. The proposed extreme cases are presented. The amount of tetragonal and monoclinic grains is only a schematic, not a quantitative representation.

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