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Effect of Nb and Fe on damage evolution in a Zr-alloy during proton and neutron irradiation

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Abstract

Detailed analysis was carried out on proton and a neutron irradiated Nb-containing Zr-alloy to study the evolution of dislocation loop size and densities as well as the formation and evolution of irradiation-induced precipitation/clustering. The results obtained here have been contrasted against previously published work on a Nb-free Zr-alloy [1, 2] to investigate the mechanistic reason for the improved resistance to irradiation-induced growth of Nb-containing Zr alloys. The combined use of bright field scanning transmission electron microscopy, ultra-high-resolution energy dispersive spectroscopy and atom probe tomography analysis provides evidence of evenly distributed

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radiation-induced Nb clusters that have formed during the early stage of proton irradiation and Fe-rich nano-rods near Fe-containing second phase particles. The former seems to have a profound effect on $\langle a \rangle$ loop and subsequent $\langle c \rangle$ loop formation, keeping $\langle a \rangle$ loop size small but number density high while $\langle c \rangle$ loops seem to initially form at similar dose levels compared to a Nb-free alloy but $\langle c \rangle$ loop line density does not increase during further irradiation. It is hypothesized that the formation of the Nb nano-precipitates/clusters significantly hinders mobility and growth of $\langle a \rangle$ loops, resulting in a small size, high number density and limited ability of $\langle a \rangle$ loops to arrange along basal traces compared to Nb-free Zr-alloys. It is suggested that it is the limited $\langle a \rangle$ loop arrangement that slows down $\langle c \rangle$ loop formation and the root cause for the high resistance of Nb-containing Zr-alloys to irradiation-induced growth.

Key words: Low-Sn ZIRLO™; Atom probe tomography; TEM; radiation induced precipitation; clusters; dislocation loops; breakaway growth

1. Introduction

Zirconium alloys are widely used as cladding materials in nuclear reactors due to their low thermal neutron absorption cross section, suitable resistance to corrosion during normal operating conditions and suitable mechanical properties at operating temperatures. Single crystal zirconium experiences a change in shape during neutron irradiation, where the crystal elongates along the $\langle a \rangle$ axis and shortens along the $\langle c \rangle$ axis without a significant change in volume [3]. This phenomenon is called irradiation-induced growth (IIG) and is observed in Zr-based components, such as fuel cladding, channel boxes and guide tubes, due to

the strong crystallographic texture of these components generated during processing resulting in macroscopic growth strain along the axial direction and shrinkage in the radial direction of a fuel clad [4]. Whilst in recrystallised Zr-alloys the initial IIG strain is low, typically in the range of 0.1%, at high fluences accelerated growth rates, so-called breakaway growth, might be observed, which limits the lifetime of fuel assemblies [5, 6].

Irradiation-induced growth is well correlated to the evolution of dislocation loops in the material. At low fluences, irradiation-induced point defects collapse into vacancy and interstitial <a>-type dislocation loops on mostly first order prismatic planes with a Burgers vector of $b = \frac{1}{3}\langle 11\bar{2}0 \rangle$ [7]. Upon further irradiation, <c>-component vacancy dislocation loops form on the basal plane, which have a Burgers vector of $b = \frac{1}{6}\langle 20\bar{2}3 \rangle$ [8]. Whilst the mechanisms of irradiation-induced growth and their correspondence to these dislocation structures are not yet fully understood, the onset of breakaway growth has often been correlated with the appearance of <c> loops although the nucleation mechanism of these type of loops remains elusive [8-12]. Hence studying the onset and cause of <c> loop formation is central to understanding breakaway growth.

Further, alloy chemistry can significantly alter the observed irradiation-induced growth and particularly the point at which breakaway growth occurs. In this context, the role of Fe has been investigated with particular interest, as Fe dissolves from pre-existing second phase particles (SPPs) during irradiation and is a fast diffusing element in Zr, potentially sitting interstitially within the Zr lattice [10, 13, 14] and interacting with point defects generated during irradiation [15 149–175]. Previous research has suggested that an increased interstitial solute

content in the Zr matrix correlates to the formation of $\langle c \rangle$ loops and as such to the breakaway growth [8, 13]. However, Fe has been found to form clusters or precipitates and segregates to $\langle a \rangle$ and $\langle c \rangle$ loops [2, 13, 16, 17]. As $\langle c \rangle$ loops are frequently found near Fe-containing SPPs, Fe has been suspected to intensify the breakaway growth phenomenon. More recently, however, increasing the Fe content in Zr-Nb-Sn-Fe alloys has been correlated with improved resistance to irradiation growth [10].

Another important alloying element in some Zr-alloys is Nb, which has been shown to improve the performance of zirconium alloys regarding corrosion and dimensional stability [18-21]. Delayed $\langle c \rangle$ loop formation has been reported for Nb-containing alloys such as E635 (Sn 1.1-1.4%, Nb 0.9-1.2% and Fe 0.3-0.47%) and M5® (Nb 0.8-1.2%). Irradiation-induced Nb clusters and nano-precipitates are often observed in such alloys, but their effect on the evolution of the dislocation structures, and hence breakaway growth, is not well understood [22].

The effect of Tin on irradiation growth is strongly dependent on irradiation temperature and at lower irradiation temperatures it is believed to be accountable for the rapid near-saturation of growth in Zircalloys, while at higher temperatures continued growth was reported [23].

The Zr-Nb-Sn-Fe alloy ZIRLO® was developed empirically in order to improve on the corrosion behaviour of Zircalloys [24-26]. For further improvements of corrosion performance, the tin content has been lowered resulting in Low-Sn ZIRLO™, which is the focus of the present work [27, 28]. Apart from the improved in-reactor corrosion resistance, the ZIRLO® family also

exhibits improved resistance to breakaway growth compared to the Zircaloy family [21, 29]. To date, very limited work has been published on the microstructural evolution of ZIRLO®-type alloys during irradiation [30] resulting in a lack of understanding of their improved irradiation growth resistance. The present study aims to elucidate the changes in the microstructure of Low-Sn ZIRLO™ as a result of irradiation through detailed analysis of the evolution of dislocation loop structure and irradiation-induced precipitation. As the availability of neutron irradiated material was limited, complementary proton irradiation was carried out under controlled low-dose conditions, which has been shown to result in similar defect evolution as neutron irradiation in Zirconium alloys [1, 31-34].

2. Experimental methods

2.1. Material

The material investigated here was fully recrystallised Low-Sn ZIRLO™ (1wt% Nb, 0.7wt% Sn, 0.1wt% Fe) that had been supplied by Westinghouse Electric Company processed following the route previously detailed in [35]. Material irradiated for 5 annual cycles at the Oskarshamn 3 nuclear power plant (burnup 49 MWd/kgU) was available for this study, which had reached a fast neutron fluence of $8.9\text{-}9.0 \times 10^{25} \text{ n/m}^2$ equating to about 18 dpa (displacements per atom) assuming a conversion of $5 \times 10^{24} \text{ n m}^{-2} \text{ dpa}^{-1}$ [36, 37]. In addition, bars of $2 \times 2 \times 20 \text{ mm}^3$ from non-irradiated Low-Sn ZIRLO™ were carefully prepared to achieve perfect mirror finish on one of the normal direction (in respect of rolling direction) faces. These samples were irradiated at Michigan Ion Beam

Laboratory's 1.7 MeV Tandetron acceleration facility with 2 MeV protons at 350 ± 9 °C using a current of $\sim 0.2 \mu\text{A mm}^{-2}$. Three sets of samples with different dose levels were achieved and their damage profile determined using the Kinchin and Pease damage calculation within the SRIM software as suggested by Stoller et al. [38]. For simulating the damage profile pure amorphous Zr using a displacement energy for Zr of 40 eV was assumed [39]. TEM samples were obtained at a depth of $\sim 12 \mu\text{m}$, where the calculated damage rate was $\sim 6.7 \times 10^{-6}$ dpa/s. For the three irradiated bars, the nominal values were 2, 5 and 7 dpa. The SRIM-calculated damage profile of the 2 dpa sample and the position of TEM thin foils is shown in Fig. 1. The atom probe tomography (APT) samples were taken close to the surface of the irradiated bar as shown in Fig. 1 and thus represent lower damage levels of 1, 3 and 4 dpa respectively, corresponding to 50-60% of the damage levels of their respective TEM samples from the same bar. Throughout the text, aforementioned dpa values will be used corresponding to the characterization method discussed.

2.2. Sample preparation for TEM and APT

For TEM examinations the proton irradiated bars were ground from the non-irradiated surface to a thickness of $\sim 150 \mu\text{m}$, before 3 mm disks were punched out. The disks were electropolished in a Tenupol-5 twin jet electropolisher with Julabo FP50 cooling unit using an electrolyte of 10% perchloric acid and 20% 2-Butoxyethanol in ethanol [31] at 0 °C and 22 V. Firstly, the disks were polished for 10-15 seconds from both sides in order to reach a depth of $\sim 12 \mu\text{m}$ from the original, irradiated surface. The depth to which the material was electropolished was monitored using a $\mu\text{scan}^{\text{®}}$ nanofocus laser

profiler. The material was then electropolished further from the non-irradiated surface to electron transparency while the polished, irradiated surface was protected with a Lacomit varnish to prevent further removal of material from this side. Subsequently the varnish was dissolved in acetone.

TEM disks of the neutron-irradiated samples were prepared by Studsvik Nuclear Company (Sweden). The tube material was sectioned and then ground to a thickness of 150 μm before 3 mm disks were punched from the material. Electropolishing of the 3 mm disks was performed using a Struers Tenupol Twin-Jet electropolisher with a solution of 10% perchloric acid in methanol at -40 °C and 20 V.

Atom probe tips were prepared from the proton-irradiated and non-irradiated samples by focused ion beam (FIB) lift-out technique using an Omniprobe micromanipulator fitted FEI Quanta 3D dual beam instrument. The samples were made at roughly 0.5 μm depth from the bulk sample surface. The detailed procedure for the tip preparation with FIB is described elsewhere [40]. The annular milling of the tips was carried out with 30 kV Ga ion-beam in multiple steps, reducing the beam current in each milling step approaching the required tip radius (~ 50 nm). The prepared tips were given a surface cleaning treatment with low energy (5 kV and 2 kV) ion beam to remove any Ga ion-beam induced artefacts and damaged layer.

2.3. Electron microscopy

The dislocation structures and redistribution of the alloying elements as a result of irradiation were studied by scanning transmission electron microscopy using an aberration-corrected (probe) FEG-STEM equipped with a high-resolution

EDS spectrum imaging system (FEI Titan G20 80-200 kV S/TEM “ChemiSTEM™”) comprising of a high brightness X-FEG source and four EDS detectors with a total collection angle of 0.7 sr located in close proximity to the sample. Bright-field STEM imaging and EDS spectral imaging was carried out at 200 kV operating voltage and with a probe current of 0.6 nA. Images of the $\langle a \rangle$ -type dislocation loops were taken on the $\langle 11\bar{2}0 \rangle$ zone axis as well as under $g_{10\bar{1}1}$ systematic row of excitations. The $\langle c \rangle$ dislocation loops were imaged using g_{0002} systematic row of excitations. For good statistics of loop size and density about 200 $\langle a \rangle$ loops were measured from at least 5 images. Since the $\langle c \rangle$ loops were not densely distributed, lower magnification images were used for their measurement. The sample thickness in the imaged areas was determined by assessing the intensity variations in convergent beam electron diffraction (CBED) patterns [41] with an associated uncertainty usually estimated conservatively to be ± 10 [42, 43]. The authors did not have any difficulties setting up the microscope in two-beam condition with discs large enough and with a good enough disc separation to accurately determine the Pendelösung fringe’s separations. Irradiated samples contain a substantial amount of damage which can make it difficult to observe the fringes. This method is also difficult to use on very thin specimens (less than around 100 nm), which restricts the accessible regions of the foil. However, both these issues were not encountered in the current work.

The $\langle a \rangle$ loop dislocation density in the neutron irradiated material was determined by Studsvik Nuclear Company. A JEOL 2100F FEG-TEM operating at 200 kV was used to image the dislocation structures in BF mode at the diffraction condition with $g_{10\bar{1}1}$ systematic row of excitations. The average loop size was calculated by measuring the loop line length of each individual segment and divide

this number by the number of loops measured. The loop number density was calculated as the number of loops per volume foil (m^{-3}) and the loop line density as the loop line length per volume foil (m/m^3). The sample thickness was determined by the t/λ method using EELS spectra [44-46]. The EELS method used in the current work was the log-ratio technique ($t/\lambda = \log(I/I_0)$). The main uncertainty from this method comes from the mean free path value for inelastic scattering for Zr (λ), which is known to an accuracy of around 5-10%. The deconvolution and integration of the zero loss peak (I_0) and the integration of the entire EELS spectrum (I) may of course also add some additional uncertainty to the thickness determination but the authors judge that this contribution should be very small when calculating the foil thickness (t).

It is worth noting that the microscopy work was performed on different samples at different microscopes, operators and following different methods for thickness measurement. While care was taken to ensure that the overall methodology was consistent between the teams, the approach here might have resulted in increased uncertainties when comparing the neutron and proton irradiated sample microstructures.

2.4. Atom probe tomography

The analysis was performed on the annular milled and cleaned sharp tips mounted on silicon coupons employing a Cameca LEAP 3000X HR™. With the sample held at 50 K, a green laser of energy 0.4 nJ and pulse frequency of 200 kHz was applied to produce pulsed field evaporation. The reconstruction of data was carried out using Cameca IVAS™ 3.6.8 software. Secondary electron (SE) images of the tips were used as a radius profile for reconstructing the atom probe data.

Iso-concentration surfaces defined by a concentration of 1 at. % Nb or 1 at. % Fe were applied to all the data sets to visualize segregation and precipitates. The threshold was chosen by the values of Fe and Nb where the cluster sizes are approximately represented by the iso-concentration surfaces. Volumes occupied by the iso-concentration surfaces are only considered for visual indications of the distribution of clusters and it is worth mentioning that their volume is not directly considered as cluster size.

For statistical analysis, individual solute clusters in the atom probe tomography (APT) reconstruction were identified using the Maximum Separation algorithm. Nearest neighbour distribution (NND) analyses underpinned optimization of the algorithm parameters: maximum separation distance, $d_{\max}$, and minimum cluster size $N_{\min}$. The maximum separation distance $d_{\max}$ was optimized based upon analysis of the distribution of first nearest neighbour distances, d_{pair} , between alike ions and applied individually to each relevant solute element. The optimal $d_{\max}$ value was estimated as the d_{pair} distance just greater than that corresponding to the peak count of the nearest neighbour distribution, but less than the d_{pair} for the peak value of the corresponding random comparator nearest neighbour distribution. The cluster size distribution function applied to the experimental and randomized data, respectively, was used to estimate the minimum number of ions $N_{\min}$ incorporated in the clusters for a given $d_{\max}$ i.e. the minimum size of clusters not expected to be observed in statistically significant numbers in a complementary homogeneous system. Each dataset was analysed independently and the $N_{\min}$ varies between 10-12 solute ions between datasets, while the $d_{\max}$ values varied between 1 and 1.5 nm. Additionally, during cluster analysis an erosion width equal to 90% of $d_{\max}$ was applied to specify the distance

from the core of the cluster for the removal of any non-clustered matrix ions. Field evaporation of Sn was affected by the laser induced surface diffusion and the Sn ions have been observed to follow preferred crystallographic poles, due to which Sn segregation is not taken in to the calculations. In the mass spectrum, there is a possibility of overlapping peaks from Nb ions and ZrH compound ions around the theoretical peak positions 91.91, 46.5 and 31.0 Da. Nb was assumed to be responsible for peaks at 31.0 and 92.97 Da, whereas the other possible position at 46.5 Da was not considered as a Nb peak for calculations, since the peak intensity at this position was relatively similar in amplitude to the neighbouring peaks which originate from Zr and ZrH.

3. Results

Fig. 2 shows an overview HAADF-STEM image of the microstructure of the Low-Sn ZIRLO™ alloy prior to irradiation highlighting β -Nb and Zr-Nb-Fe SPPs, which were characterized by EDS spectral imaging.

Table 1 lists the analysed samples and their dislocation sizes and densities for a direct comparison. The BF-STEM images presented in Fig. 3 describe the evolution of $\langle a \rangle$ dislocation loops in the material during proton irradiation to 2 dpa and 5 dpa (Fig. 3 a and b) and neutron irradiation to 18 dpa. The images were taken on the $\langle 11\bar{2}0 \rangle$ zone axis. As the damage level increases, the $\langle a \rangle$ -type dislocation loops become smaller, but their density seems to rise. The average $\langle a \rangle$ loop diameter and $\langle a \rangle$ loop number density for Low-Sn ZIRLO™ is compared in Fig. 4 to data for the Nb-free Zircaloy-2 [2]. It is worth noting that the compared Zircaloy-2 material was irradiated under similar experimental conditions and to

similar fluences detailed in this study. The size of the $\langle a \rangle$ -type dislocation loops is smaller for Low-Sn ZIRLO™ than for Zircaloy-2 after proton irradiation to the same damage levels, but the number density is higher. The higher number density of $\langle a \rangle$ -type dislocation loops is also found when comparing the neutron irradiated Low-Sn ZIRLO™ to Zircaloy-2, whilst the $\langle a \rangle$ loop diameter converges towards 4 nm for both alloy systems.

Fig. 5 shows BF-STEM images of the microstructure of Low-Sn ZIRLO™ after proton irradiation to 5 dpa and 7 dpa as well as neutron irradiation to 18 dpa using systematic row of excitations g_{0002} , under which c-component loops become visible. The lowest proton dose at which c-component loops were observed was ~ 5 dpa, which is the same as for the Nb-free Zircaloy-2 [2], but a lower density of $\langle c \rangle$ loops were found in the neutron irradiated Low-Sn ZIRLO™ material despite the much higher damage level. The comparison of the average $\langle c \rangle$ loop diameters in Low-Sn ZIRLO™ and Zircaloys presented in Fig. 6a highlights that the $\langle c \rangle$ loops in Low-Sn ZIRLO™ are smaller than the ones in Zircaloy-2 [2] and Zircaloy-4 [47], especially after proton irradiation to the same dose level. Regarding the $\langle c \rangle$ loop number densities, plotted in Fig. 6b, the initial value at 5 dpa (proton irradiation) is higher for Low-Sn ZIRLO™ than for Zircaloy-2, but after continued irradiation the $\langle c \rangle$ loop densities remains constant for Low-Sn ZIRLO™ while it rises dramatically in Zircaloy-2 for both proton and neutron irradiation.

The EDS chemical maps in Fig. 7 provide evidence of irradiation-induced precipitation or clustering of Nb and Fe already formed after 2 dpa proton irradiation. Rod shaped Fe-rich precipitates are readily observed under a two beam condition with $g=[0002]$ [48] close to the $\langle 11\bar{2}0 \rangle$ zone axis, usually in the

vicinity of Fe-containing SPPs (Fig. 7 a and b). They are ~ 8 nm long and orientated at $15\text{-}20^\circ$ off the $[0002]$ direction. The Nb-rich clusters or precipitates become visible under a strong $g=[0002]$ condition and are homogeneously distributed throughout the matrix irrespective of the distance to SPPs. Though most of the Nb-rich clusters appear spherically shaped with roughly 5 nm diameter, some of them appear elongated along the trace of the basal plane with a length of about 8 nm.

Fe- and Nb-rich clusters or precipitates are also observed in the material after 5 dpa proton irradiation as shown in Fig. 8. The Fe-rich precipitates shown in Fig. 8a and 8b are of similar shape and size and mainly present close to Fe-containing SPPs, as was seen in the material after 2 dpa proton irradiation. The Nb-rich clusters shown in Fig. 8c and 8d also appear very similar to the clusters after 2 dpa, but more clusters appear now elongated along the trace of the basal plane. It is worth noting that the $\langle c \rangle$ component loops that have their habit plane on the basal plane appear most frequently in close vicinity to the elongated Nb clusters. This observation might suggest that the Nb clusters have some association with $\langle c \rangle$ component dislocation loops but more work is needed here to provide evidence.

The observations based on the EDS chemical maps are confirmed by the results of atom probe tomography carried out on the samples corresponding to the 2 dpa and 7 dpa TEM samples of proton-irradiated low-Sn ZIRLO™, compared to the non-irradiated (0 dpa) sample which are presented in Fig. 9. The reader is reminded though that due to the different location from which the atom probe samples were extracted (Fig. 1), the irradiated samples now correspond to 1 dpa (Fig. 9b) and 4 dpa (Fig. 9c). Again, Nb and Fe are seen to cluster as a result of

proton irradiation. The atom probe tomography results also show Fe clusters to be mainly rod shaped and their long axes are aligned in specific direction after 1 dpa proton irradiation as seen in Fig. 9b. As it was suggested by the EDS chemical maps, the Fe clusters observed by APT are not found throughout the matrix, but are limited to some volume within the material. After 4 dpa proton irradiation the Fe clusters appear more evenly distributed and no longer rod shaped or aligned in a particular direction or plane as shown in Fig. 9c. The Nb-rich clusters are homogeneously distributed after even 1 dpa as well as 4 dpa proton irradiation. The APT data suggests some preferred orientation of Nb rich clusters after 1 dpa proton irradiation, but at 4 dpa this is no longer found. The analysis of the non-irradiated sample confirmed that the observed clustering is due to proton-irradiation and not a sample preparation artefact, as illustrated by the iso-concentration surface construction shown in Fig. 9a. Fig. 9c also shows a lack of Nb clusters in the vicinity of a beta-Nb particle after irradiation. This suggests that the Zr-matrix is not supersaturated with Nb very close to beta-Nb particles, probably due to the lower diffusivity of Nb as suggested by Doriot et al [49].

Quantification of the number of clusters and their respective size due to 1 and 4 dpa proton irradiation was extracted from the APT data, the results of which are presented in Fig. 10. For each dose level, volumes consisting of roughly 34 million atoms were considered. In the case of 4 dpa, this was a single APT reconstruction, while three individual data sets were combined to reach 34 million atoms for the 1 dpa sample. Fig. 10a shows that the number of Fe clusters or precipitates increases from ~50 clusters to ~230 clusters, within comparable analysis volumes, and the volume fraction and number density of Fe rich clusters has increased from 0.18 % to 0.21% and $2.72\text{e}^{22} / \text{m}^3$ to $2.61\text{e}^{23} / \text{m}^3$ respectively

when the dose increases. The maximum size of the clusters remains unchanged by the damage level. Hence, there is mainly an increase in the number of very small clusters rather than a growth of existing clusters with increasing dpa level. In contrast, the number of Nb rich clusters (Fig. 10b), ~130 clusters, is significantly greater than the number of Fe clusters at 1 dpa, but at 4 dpa there are fewer Nb clusters (~200 clusters) than Fe clusters. The increase in damage did not result in a significant increment in the number of Nb clusters, while comparing with the Fe clusters. Similar to the Fe rich clusters, Nb rich clusters exhibit an increase in volume fraction from 0.26 % at 1 dpa to 0.30 % at 4 dpa. Their number density also increases from $7.32 \times 10^{22} / \text{m}^3$ for 1 dpa to $2.23 \times 10^{23} / \text{m}^3$ for 4 dpa samples. The maximum observed cluster size increases significantly with dose for the Nb-rich clusters unlike the Fe-rich clusters. The Nb clusters have 31.82 ± 1.32 % Nb in the 1 dpa samples and 29.53 ± 1.39 % Nb in the 4 dpa samples. These values might be affected by the difficulty in deconvolution of peaks of Nb when there are ZrH peaks overlapping. But it is interesting to note that the average Nb content is not varying much with the dose. In all the datasets presented in Fig. 10, pre-existing SPPs were eliminated from the statistical analysis.

Using the APT data of the non-irradiated, 1 dpa and 4 dpa samples, the α -Zr matrix composition was analyzed for the material volume devoid of clusters and precipitates of Fe and Nb. The sample volume investigated here was equivalent to that used for data presented in Fig. 10. Fig. 11 shows the matrix concentration of Fe and Nb in these three conditions. The error bars represent standard errors calculated from standard deviation of multiple datasets, not given for 4 dpa since this condition has a single large dataset. The atomic percent of Fe in the α -Zr matrix increases with increasing dose from the non-irradiated state to

4 dpa at which point the Fe concentration has doubled (from 0.02 to 0.043 at%). Conversely, the α -Zr matrix concentration of Nb decreases with increase in damage level, with a dramatic drop between non-irradiated condition and at 1 dpa and a much smaller further decrease at 4 dpa. It should be noted that the Nb content in the matrix, excluding clusters in the non-irradiated condition is surprisingly low (~ 0.07 at. %) considering that usually a solubility limit of 0.2 – 0.5 wt.% is quoted for Zr [50] in binary Zr-Nb alloys. Whereas, the total atomic fraction of Nb in the analysed volume, excluding SPPs but including all the clusters, is ~ 0.1 at 1 dpa and it is only 0.07 at 4 dpa (not illustrated). However, no comparative results are available in open literature for more complex Nb-containing commercial Zr-alloys. It is important to note that due to overlapping peaks of Nb and ZrH it cannot be ruled out that the Nb fraction obtained from the mass spectrum analysis is slightly underestimated.

4. Discussion

4.1. Evolution of <a>-type dislocation loops

Fig. 3 and 4a show a similar trend for the size evolution of <a>-type dislocation loops in Low-Sn ZIRLO™ when comparing proton and neutron irradiation with <a> loop size reducing with increasing dose levels reaching a minimum value of about 4 nm. In Fig. 4 the <a> loop size and number density of <a> loops in Low-Sn ZIRLO™ are plotted together with data published previously on Zircaloy-2 [2]. In contrast to Zircaloy-2, Low-Sn ZIRLO™ contains Nb, which is a slow diffusing substitutional alloying element among the major alloying elements in zirconium [51, 52]. Numerous research has demonstrated that Nb

containing Zr-alloys display significantly lower IIG than Nb-free Zircalloys [18-21], but the reason for this improvement is not yet understood. Considering the evolution of dislocation loops during irradiation, Fig. 4a and b demonstrate that in both alloys the $\langle a \rangle$ loop size initially decreases while the dislocation number density goes up with increasing dose. It is interesting to note that at the lowest dose observed by TEM (2 dpa) Low-Sn ZIRLO™ already displays a loop size comparable to Zircaloy-2 after 5 dpa while the dislocation number density is comparatively high. Generally, it can be expected that an initial low number density results in reduced strain field interaction between loops allowing them to grow. However, as shown in Fig. 7c, d and Fig. 9b for Low-Sn ZIRLO™, and also demonstrated for other Nb-containing Zr-alloys [49], a large number of Nb clusters are readily formed throughout the matrix during the early stage of irradiation, also evidenced by the observed reduction of Nb dissolved in the Zr matrix in Fig. 11. The early formation of Nb clusters might limit $\langle a \rangle$ loop growth from a very early stage although it is also possible that already Nb in the matrix has a pinning effect by affecting the core structure of the dislocations. The lower interaction of these small loops would also make it easier for the number and line density of dislocation loops to rapidly increase.

The role of a high $\langle a \rangle$ dislocation density on breakaway growth has been discussed previously in the light of the difference in diffusional anisotropy (DAD) theory proposed by Woo [53]. A high density of $\langle a \rangle$ loop dislocations is speculated to result in low growth, as $\langle a \rangle$ loops will act as the dominant sink for point defects, but only have a small bias towards which type of point defects are annihilated [54], as opposed to $\langle c \rangle$ component loops, which only form vacancy loops.

It is also interesting to compare the present data with observations obtained on neutron irradiated E635 with a composition Zr-1Nb-1.2Sn-(0.15-0.65)Fe wt.%, i.e. higher Sn and Fe content than Low-Sn ZIRLO™, irradiation temperatures 300-420 °C [18, 29]. The average $\langle a \rangle$ loop size was reported to be 9 – 12 nm, i.e. larger than in Low-Sn ZIRLO™, while the loop line density was lower. These works also showed banding of $\langle a \rangle$ loops, which seems to be more developed than in the present work. In a similar alloy, Zr-1Nb-1Sn-0.4Fe wt.%, the $\langle a \rangle$ dislocation loop size was reported to increase slightly during the course of neutron irradiation from 0.2 dpa to 16 dpa by Nikulina [55], in contrast to the observations made here, and the highest $\langle a \rangle$ loop number density was found at 0.2 dpa. Shishov et al. compared E635 with E110, which contains 1 wt.% Nb and no other alloying elements, and concluded that the addition of Fe and Sn to a Nb-containing alloy results in a stronger alignment of the $\langle a \rangle$ dislocation loops [22]. Shishov in another article on the similar type of alloys, reported that the content of Fe and Sn decreases the $\langle c \rangle$ loop density by ordering $\langle a \rangle$ loops and ordering the irradiation induced precipitates [56]. They have also claimed that the stress and the Fe content control the distribution of the precipitates. Presence of Sn has been speculated as the cause of alignment or banding of $\langle a \rangle$ loops in Zircaloy-2 [2], based on the observation of anti-correlative alignment of Sn segregation with $\langle a \rangle$ -loops, but their sequence of formation is not evident. With reference to Nb and lower level of Sn in Low-Sn ZIRLO™ compared to Zircaloy-2 [2], it appears that the presence of large number of Nb clusters could arrest the movement of $\langle a \rangle$ -loops against their alignment, whereas the role of Sn in enhancing the tendency of aligned dislocation $\langle a \rangle$ loops is not clear. The differences in the characteristics of the $\langle a \rangle$ loop evolution between E635 and Low-Sn ZIRLO™ cannot be easily

explained, but highlight the complexity of the interplay of the different alloying elements during irradiation.

4.2. Evolution of c-component loops

As mentioned earlier, previous research has demonstrated that Nb-containing Zr-alloys show delay in breakaway growth or significantly reduced breakaway growth compared to Zircalloys [18-21, 29]. Therefore, one might assume that $\langle c \rangle$ loop nucleation is also delayed by Nb additions. However, Fig. 6 shows that in the case of proton irradiation, $\langle c \rangle$ loops can be observed in Low-Sn ZIRLO™ and Zircaloy-2 after 5 dpa. Indeed, at this stage the $\langle c \rangle$ loop number density is greater for Low-Sn ZIRLO™ than Zircaloy-2. However, at 7 dpa the number density has not changed for Low-Sn ZIRLO™ whereas for Zircaloy-2 it has increased dramatically. Further, Fig. 6b suggests that for both alloys proton irradiation enhances $\langle c \rangle$ loop formation compared to neutron irradiation. Clearly, there are very few data points from the proton irradiation experiments to draw conclusions, however, the data suggest that while Nb might not delay the onset of $\langle c \rangle$ loop formation, it does slow down a further increase in $\langle c \rangle$ loop density. In principle, similar observations have been obtained by Doriot et al. for Zr-1Nb (M5) and other Zr-Nb-Sn-Fe alloys similar to Low-Sn ZIRLO™ [54]. This work has also shown that the onset of $\langle c \rangle$ loop formation is not necessarily associated with immediate breakaway growth. They argue that a critical $\langle c \rangle$ loop density needs to be established before $\langle c \rangle$ loops become a dominant sink for vacancies and breakaway growth starts. The initial formation of $\langle c \rangle$ loops is usually seen near SPPs [57], which in the case of [54] also includes Zr-Nb-Sn-Fe alloys. Hence, it might not be so surprising that Low-Sn ZIRLO™ containing similar type of SPPs

does not display any delay in $\langle c \rangle$ loop formation compared to Zircaloy-2. The low number density of $\langle c \rangle$ loops as irradiation proceeds might again be explained directly or indirectly by the presence of irradiation-induced Nb-clustering. For Zircaloy-2 a correlation has been demonstrated previously between alignment of $\langle a \rangle$ loops along basal traces and the formation of $\langle c \rangle$ loops [2]. In Low-Sn ZIRLO™ such $\langle a \rangle$ loop alignment is clearly less developed (compare Fig. 3 with Fig. 3 in [2]), which could explain why the $\langle c \rangle$ loop density remains comparatively low. The less pronounced $\langle a \rangle$ loop alignment in Low-Sn ZIRLO™ could be explained by the presence of Nb clusters reducing any level of mobility of the $\langle a \rangle$ loops and therefore stopping them from aligning in the most energetically favourable configuration. It is also notable that the proton-irradiated Low-Sn ZIRLO™ shows $\langle c \rangle$ loops only half the size of those observed for proton-irradiated Zircaloy-2, see Fig. 6a. This trend is less pronounced for the neutron-irradiated material but still present and might be equally be explained by the even distribution of irradiation-induced nano-clusters observed by high resolution EDS and APT analysis in Fig. 7, 8, 9 and 10.

4.3. Irradiation-induced precipitation of Nb and Fe

Irradiation-induced precipitation/clustering of Nb and Fe is observed here in proton-irradiated Low-Sn ZIRLO™. Although both elements have been observed previously to form precipitates or clusters during irradiation [16, 18, 22, 57, 58] this is the first time that radiation-induced Fe precipitation has been reported in Zr-Nb-Sn-Fe type alloys. This might be due to the small nature, morphology and orientation of the Fe particles, which means they can be easily confused with $\langle a \rangle$ loops and evidence can only be provided by the application of ultra-high-

resolution EDS spectral imaging and atom probe tomography analysis. In addition, they might not be found throughout the material, but only in the vicinity of Fe-containing SPPs.

Fig. 10 shows that even at the lowest dose level the number of Nb clusters is far greater than the number of Fe precipitates. It should be noted that it is not known whether the analysed APT volumes were originally in close proximity to a SPP. However, the ultra-high-resolution EDS analysis suggests that Fe precipitates are mainly found near Fe-containing SPPs at low dose whereas Nb clusters are seen far more evenly spread. As Nb is a slow diffusing alloying element in zirconium [51, 52, 59], the large number of evenly distributed Nb clusters at 1 and 2 dpa suggests that the α -Zr matrix was still supersaturated with Nb prior to irradiation. Accordingly, Fig. 11 suggests that the Nb content in the matrix does continuously reduce from 0 to 4 dpa. A surprising aspect of Fig. 11 is the very low Nb content (0.07 at. %) before irradiation. However, whilst a number of publications have stated the solubility limit of Nb in Zr to be between 0.2 % – 0.5 % in binary model alloys [50, 60], such values have never been confirmed experimentally in commercial alloys. However, there is a possibility in the APT analysis of Nb ions being missed due to overlapping peaks with ZrH peaks in the mass spectrum giving a systematic error (underestimating Nb content). In [54] the number density of neutron irradiation-induced Nb clusters in the Zr-Nb-Sn-Fe alloys (similar to Low-Sn ZIRLO™) were reported to be mostly independent of fluence level or variations in the alloy composition at high fluences. In the present study at low proton fluences, APT results suggest that there is an increase in the number of particles observed when the damage level is increased from 1 to 4 dpa using (Fig. 10b). Also, the cluster size (number of ions in clusters) has increased

between 1 dpa and 4 dpa, which indicates that the Nb-clusters have grown. A normalized frequency distribution of size of Fe and Nb cluster is given in the supplementary Fig. S1, which gives indication of a bimodal distribution of Nb clusters at 4 dpa. Considering the small volume studied by APT, it is difficult to be certain that these are real trends or related to statistical variations.

The precipitation of Fe into rod-shaped particles during proton-irradiation has been observed previously for Zircaloy-2 and a binary Zr-Fe alloy [16]. Topping et al. showed that Fe first segregates to $\langle a \rangle$ loops at low dose and forms precipitates upon further irradiation [16, 58]. In Zircaloy-2 the length of the Fe rods drastically decreases from 23 nm to 7 nm between proton-irradiation to 2 and 5 dpa [58], which is not observed in Low-Sn ZIRLO™. This difference seems to be related to the evolution of the average $\langle a \rangle$ loop size for this dpa range, which also decreases for Zircaloy-2 but not for Low-Sn ZIRLO™, see Fig. 4a. Consequently, in Low-Sn ZIRLO™ with increasing dose the number of Fe rods goes up but the rods do not grow, as demonstrated in Fig. 10. Whilst much of the Fe seems to segregate to clusters, Fig. 11 suggests that the Fe content in the matrix increases with dose and that it assumes a similar value to that of Nb. This is an interesting observation as it could have significant impact not only on growth but also creep since Fe is a very fast diffusing element and aqueous corrosion since more evenly distributed Fe may dope the oxide affecting its conductivity.

The two types of irradiation-induced precipitates/clusters found in Low-Sn ZIRLO™ may act as sinks for point defects. It is interesting to note that the length axes of these two types of precipitates are oriented almost orthogonal to one another. Whilst the Fe rods are elongated in 12-15° to the [0001] direction in

the α grain, the Nb precipitates tend to be generally elongated along the trace of the basal plane, see for example Fig. 7. The orientation of the Nb precipitates in the matrix and the fact that they are best imaged with $g=[0002]$ has led to their confusion with $\langle c \rangle$ -component loops in the past [18], whilst the Fe precipitates seem more closely linked to the $\langle a \rangle$ -type dislocation loops [16]. This poses the question whether the precipitates interact differently with point defects. Woo discussed the possibility of diffusion anisotropy depending on the orientation of a line defect [53]. As the Fe precipitates are not evenly distributed throughout the matrix (at least during the early stages of irradiation), one might expect to see differences in the dislocation structures close to Fe-containing precipitates. An increase in $\langle c \rangle$ -component loops was indeed observed in the vicinity of the Fe-containing Laves-phase Zr (Fe,Nb)₂ SPPs by Doriot et al. in Q12™ (Zr-1Nb-0.5Sn-0.1Fe) [54] under neutron-irradiation. However, in the present work such observations were not made, possibly due to the following reason. The presence of Fe in the solid solution was proposed to enhance the vacancy diffusion along $\langle c \rangle$ axis and locally modify the c/a ratio and thus stacking fault energy leading to enhanced $\langle c \rangle$ loop formation [9]. Since the Fe was found to form numerous clusters in the Low-Sn ZIRLO™, the amount of Fe in solid solution has not increased significantly even after 4 dpa and thus did not enhance the $\langle c \rangle$ loop formation in the vicinity of SPPs. However it is important to note in this context that a limited increase in the Fe content in Zr-Nb-Sn-Fe alloys has been correlated to a decrease in the overall $\langle c \rangle$ dislocation density and a delay in breakaway growth [29].

Although the Fe-clustering is also expected to limit the formation of $\langle c \rangle$ -type dislocation loops through the control on the diffusivity of point defects, the

primary reason for the reduction in $\langle c \rangle$ loop nucleation comes from the Nb clusters, since the Fe clusters are not homogeneously distributed. As we discussed earlier, there is a correlation of $\langle a \rangle$ loop alignment in basal planes and the $\langle c \rangle$ loop formation; the reduction of such $\langle a \rangle$ loop alignment through the homogeneously distributed Nb clusters seem to have a major control over the $\langle c \rangle$ loop nucleation and thus on the potential of approaching a breakaway growth stage.

5. Conclusions

The microstructural evolution of Low-Sn ZIRLO™ during proton-irradiation was studied here by STEM in combination with EDS as well as APT and compared to neutron-irradiated Low-Sn ZIRLO™. The results are compared to a similar study performed on Zircaloy-2 (Nb-free Zr alloy) from [2]. Thereby comparing an alloy more resistant to the irradiation-induced growth phenomena (Low-Sn ZIRLO™) to one (Zircaloy-2) that shows less resistance to irradiation growth. The observations can be summarized as follows:

1. During the early stage of (proton) irradiation at 350°C $\langle a \rangle$ dislocation loops are significantly smaller and higher in density in Low-Sn ZIRLO™ compared to Zircaloy-2. Trends for proton- and neutron-irradiated material suggest that the $\langle a \rangle$ loop size converges for the two alloys at higher dpa levels to a range of about 4 nm. Limited banding of $\langle a \rangle$ loops along basal traces is observed for irradiated Low-Sn ZIRLO™, however it is far less pronounced than in Zircaloy-2.

2. Low-Sn ZIRLO™, like Zircaloy-2, shows $\langle c \rangle$ loop formation after proton-irradiation to 5 dpa. However, upon further irradiation the $\langle c \rangle$ loop density remains comparatively stable in Low-Sn ZIRLO™ while in Zircaloy-2 it increases quite dramatically. This indicates that breakaway growth might not be correlated with the onset of $\langle c \rangle$ loop formation but significant increase of $\langle c \rangle$ loop density. This hypothesis is also supported by the observation of very few $\langle c \rangle$ loops in Low-Sn ZIRLO™ irradiated to 18 dpa by neutrons.

3. Nb and Fe both form irradiation-induced clusters in Low-Sn ZIRLO™. While Nb precipitates/clusters seem to be evenly distributed in the α -matrix, Fe precipitates/clusters are mainly found near Fe-containing SPPs. Atom probe analysis suggests that with increasing dose level the number of Fe-rich precipitates/clusters increases while their size remain very small. In contrast, coarsening during continued irradiation is a more dominant feature of the Nb-rich precipitates/clusters. Analysis by APT also provides evidence that the concentration of Nb in α -Zr decreases when the material is irradiated while the Fe content in the α -Zr matrix increases slightly. It is also important to note that the Nb content in α -Zr of this alloy appears to be much lower than previously suggested, even before irradiation.

4. It is proposed that the very small $\langle a \rangle$ loop size from an early stage of irradiation and the stable and comparatively low $\langle c \rangle$ loop density in Low-Sn ZIRLO™ are related to the early formation of evenly distributed radiation-induced Nb precipitates/clusters. These precipitates/clusters may hinder $\langle a \rangle$ loop growth and the banding of $\langle a \rangle$ loops along basal traces. It is therefore hypothesized that Nb precipitates/clusters are responsible for improving resistance to irradiation-induced growth and a fundamentally important aspect for this is that the α -Zr

matrix retains a slightly oversaturated Nb content before the material goes into service.

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Tables

Table 1: Dislocation mean size and densities

Damage level (nominal)	2 dpa H+	5 dpa H+	7 dpa H+	18 dpa n
Average <a> loop diameter (nm)	5.5	4.6	Not analysed	4
Average <a> loop number density (*10 ²² m ⁻³)	0.75	1.7	Not analysed	3
Average <c> loop diameter (nm)	None	35	63	79
Average <c> loop number density (*10 ²⁰ m ⁻³)	None	1.8	2	> 0.8

Figures:

Fig. 1. Depth damage profile from the irradiated surface based on the Kinchin and Pease damage calculation within the SRIM program. The depth at which the atom probe tomography tips and TEM foils were extracted are indicated.

Fig. 2. HAADF STEM image of SPPs in Low-Sn ZIRLO™. The nature of the particles was determined by EDS spectral imaging.

Fig. 3. BF STEM images of <a>-type dislocation loops in Low-Sn ZIRLO™ taken on the $\langle 11\bar{2}0 \rangle$ zone axis; a) after 2 dpa proton irradiation, b) after 5 dpa proton-irradiation and c) after 18 dpa neutron-irradiation.

Fig. 4. a) average <a> loop diameter and b) number density of proton and neutron irradiated Low-Sn ZIRLO™ in comparison with Zircaloy-2 [2]. All the proton-irradiation dpa values have been rounded off.

Fig. 5. BF STEM images of <c>-type dislocation loops in Low-Sn ZIRLO™ taken with g_{0002} systematic row of excitations; a) after 5 dpa proton-irradiation, b) after 7 dpa proton-irradiation and c) after 18 dpa neutron-irradiation.

Fig. 6. a) average $\langle c \rangle$ loop diameter and b) number density of proton and neutron irradiated Low-Sn ZIRLO™ in comparison with Zircaloy-2 [2] and Zircaloy-4 * [47]. All the proton-irradiation dpa values have been rounded off.

Fig. 7. Radiation induced precipitation of alloying elements after 2 dpa proton-irradiation; a) BF STEM image of Fe precipitates (examples highlighted by red ellipses), g_{0002} systematic row of excitations close to $\langle 11\bar{2}0 \rangle$ zone axis, b) EDS spectral image of Fe distribution showing Fe precipitates; c) BF STEM image of Nb clusters (examples highlighted by red ellipses), g_{0002} , d) EDS spectral image of Nb distribution showing Nb clusters.

Fig. 8. Radiation induced precipitation of alloying elements after 5 dpa proton-irradiation; a) BF STEM image showing Fe precipitates near an SPP (indicated by red arrow) and the area of the spectral image (red rectangle), g_{0002} systematic row of excitations near $\langle 11\bar{2}0 \rangle$ zone axis, b) EDS spectral image of the Fe distribution showing Fe rods c) BF STEM and d) EDS spectral image of Nb distribution showing Nb clusters.

Fig. 9. Atom probe tomography reconstructed volumes of (a) non-irradiated sample showing Fe and Nb distribution (b) 1 dpa (c) 4 dpa proton irradiated samples. The iso-concentration surfaces were constructed with Nb 1% and Fe 1%. Clusters of Fe and Nb form during irradiation. Fe clusters are aligned at 1 dpa proton and often rod shaped. At higher doses, the distribution and shape of clusters is more homogeneous.

Fig. 10. Evolution of the number and size of a) Fe and b) Nb rich clusters formed during 1 and 4 dpa proton-irradiation. The volume of analysed material is roughly equal for both samples (~34 million ions). Large SPPs are presumed to be original and not included here.

Fig. 11. Concentration of Fe and Nb in the matrix (excluding SPPs and clusters) calculated from the atom probe tomography reconstructed volumes of non-irradiated, 1 dpa and 4 dpa samples (cf. 2 dpa & 7 dpa for TEM). Error bars represent standard errors from different datasets. 4 dpa has no error bar since it is from a single large data set.

Supplement:

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Caption for the supplementary figure

Fig. S1: Normalized frequency distribution of size of the Fe and Nb clusters observed in 1 dpa and 4 dpa APT samples.