XANES Study of Fe and Nb Oxidation in Zr-2.5Nb Oxide Layers

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INTRODUCTION

Zirconium alloys are used extensively in nuclear reactors particularly because of their superior corrosion resistance. These alloys form thin protective oxides that reduce the corrosion rate in reactor. Alloying elements (such as Fe and Nb) are crucial to the stability of the protective oxide, and are present in the metal both in solid solution and as intermetallic precipitates [1]. Previous research using microbeam X-ray absorption near-edge spectroscopy (XANES) has shown that both Fe and Nb atoms in zirconium alloys oxidize later than do the Zr atoms [2, 3, 4]. The oxidation state of these atoms when incorporated into the oxide layer could influence the oxidation kinetics and hydrogen pickup of the alloy by affecting the overall oxide layer conductivity and consequently hydrogen transport [2]. In this study, the oxidation of Fe and Nb in Zr-2.5Nb oxide layers is investigated using microbeam synchrotron radiation, which allows tracking of the evolution of the XANES signal as a function of distance from the metal-oxide interface, in order to understand the detailed process of the oxidation of Fe and Nb atoms in the oxide layers.

EXPERIMENTAL

The 2-ID-D beamline at the Advanced Photon Source (APS) at the Argonne National Laboratory (ANL) permits the use of tunable X-ray energy from 5-32 keV with a spot size of 0.2 µm x 0.2 µm. This allows for using XANES for the examination of the oxidation states of Fe and Nb with fine spatial resolution. The alloy of interest for this study was Zr-2.5Nb. Zr-2.5Nb has a composition of 2.4-2.8 wt.% Nb, <0.15 wt.% Fe, <0.02 wt.% Cr, and 900-1300 ppm oxygen with the remainder as zirconium [1]. A summary of the samples examined are shown in Table I.

Table I. Zr-2.5Nb samples examined using the 2-ID-D beamline at the APS in this study

Sample	Exposure Condition	Time (days)	Oxide Thickness (µm)
C1757P	360 °C water	20	1.55
C1758P	360 °C water	170	3.12
C5031P	454 °C steam	200	39.9

The samples were prepared in cross-section in the same manner as described in previous work [3]. At the beamline, each sample was attached to an aluminum stud parallel to the beam and then tilted into the beam's path. The sample was centered and the microbeam scanned across the oxide and metal. A Ge(Li) Canberra solid state detector was used to acquire fluorescence data at each scanning step. Because the zirconium fluorescence counts are less in the oxide layer than in the metal, the X-ray fluorescence (XRF) data can be used to determine the microbeam location within the oxide layer. For each scan, the sample was moved in steps of 0.25-2 µm across the oxide layer while fluorescence and XANES data were simultaneously acquired. For each sample, one full XANES scan was acquired at each location in the oxide layer. This means that the beam traversed the sample and at each stop a XANES scan near the Fe or Nb absorption edges (encompassing a range of 100 eV, from 7.078 keV to 7.178 keV for Fe and 60 eV, from 18.98/18.99 to 19.04/19.05 keV for Nb) was obtained.

The beam interaction area combined with the distribution of the second phase particles (SPPs) ensures that there is signal obtained from alloying elements incorporated in SPPs in the oxide layer [2, 3, 5]. The XANES spectra evolve in a systematic fashion as the beam travels across metal and into the oxide. To analyze this evolution quantitatively, it is necessary to use XANES standards, generated by performing a XANES scan on pure materials. Thus, XANES spectra for standards were acquired for bcc-Fe, Fe_2O_3, Fe_3O_4, $Zr(Fe,Cr)_2$, bcc-Nb, NbO, NbO_2, and Nb_2O_5 to create fluorescence plots around the Fe and Nb absorption edges. The standards were in the form of powders acquired from Alfa Aesar, and which had been used in previous studies [2, 3]. Additional Nb standards were created from the samples themselves by going far into the metal or far into oxide, where the oxidation state of the Nb was well known. The fluorescence plots obtained in the oxide layers of the alloys were then fit as a linear combination of the standards using the Demeter software package, part of the Athena Suite, to determine the percentage of Fe or Nb atoms in the alloys that were in the metallic or oxidized state [6]. Following this method, the best overall fit provided the best estimate of the fraction of Fe or Nb atoms oxidized at a particular location.

RESULTS AND DISCUSSION

Fe XANES

Examples of the Fe fluorescence spectra acquired from two of the Zr-2.5Nb samples are shown in Fig. 1.

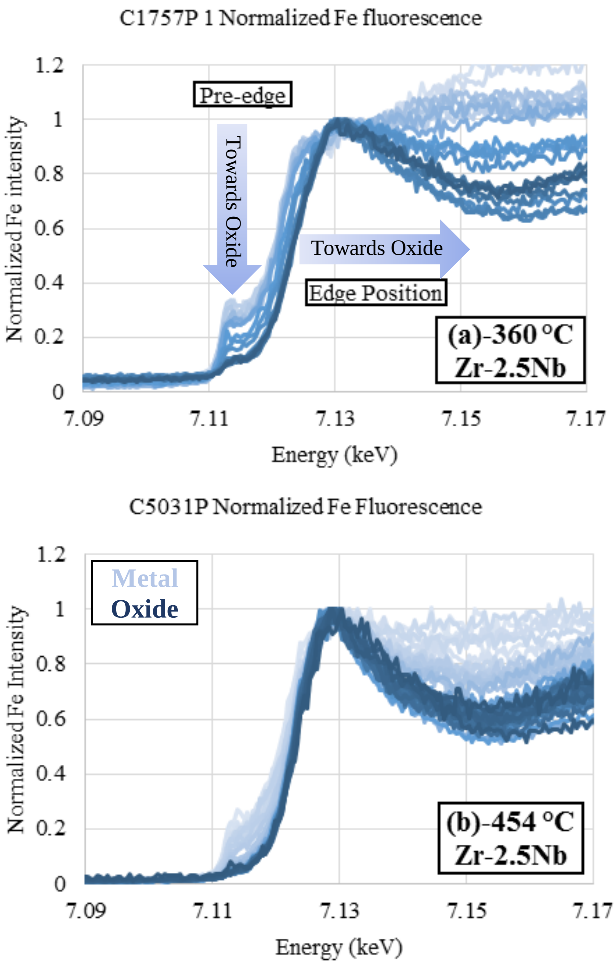

Fig. 1. (a)-(b) Examples of normalized Fe fluorescence from Zr-2.5Nb samples corroded at two different temperatures (360 °C and 454 °C)

As the scan progresses from the metal (light blue) into the oxide layer (dark blue) the spectra shift as the percentage of oxidized Fe atoms increases. As the amount of signal from oxidized Fe atoms increases, the intensity of the pre-edge feature (small peak just after 7.11 keV) decreases and the edge position (at 0.5 normalized intensity) shifts to a higher energy, as expected and as previously observed [3]. Fig. 2 shows the fraction of metallic Fe as a function of distance from the metal-oxide interface on the three Zr-2.5 Nb samples.

In the oxide layers formed on the samples corroded at 360 °C in water, the percentage of metallic Fe atoms in Zr-2.5Nb reaches close to zero in the range of 1-1.4 µm from the metal-oxide interface. For the oxide layers formed during corrosion in steam at 454 °C, the percentage of metallic Fe reaches near zero at a slightly higher distance (~2 µm) from the metal-oxide interface. This higher percentage of metallic Fe in the oxide layers formed at higher temperature has been previously hypothesized to be due to the accelerated corrosion of the Zr metal at these temperatures [3].

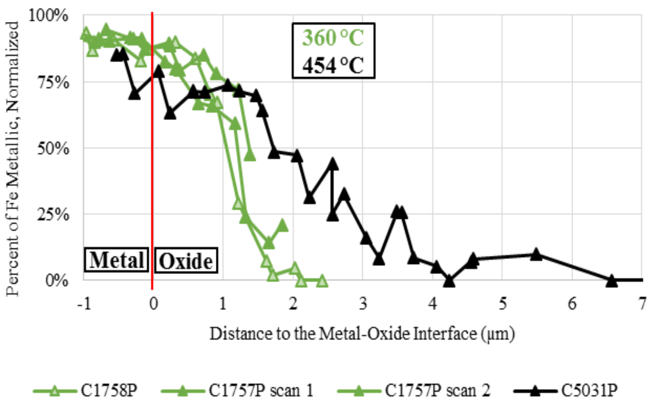

Fig. 2. Combined plot showing the percentage of metallic Fe as a function of distance from the metal-oxide interface for Zr-2.5Nb samples (360 °C in green, and 454 °C in black)

Fig. 3 shows a comparison of metallic Fe as a function of distance between scans performed on a Zircaloy-4 and Zr-2.5Nb sample at the same temperature (360 °C).

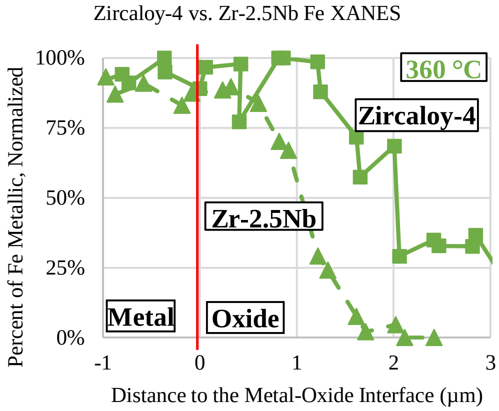

Fig. 3. Comparison of percentage of metallic Fe in the oxide layers formed in Zircaloy-4 (H1406J, 120 days, 2.09 µm) and in Zr-2.5Nb (C1758P, 170 days, 3.12 µm) as a function of distance from the metal-oxide interface for samples corroded at 360 °C [3]

The most noteworthy difference between the oxide layer formed in Zircaloy-4 and Zr-2.5Nb is that the Fe metallic fraction in the Zr-2.5Nb sample decreases to zero closer to the metal-oxide interface than in Zircaloy-4. This is likely caused by the difference in the amount of Fe in both of these alloys and how it is distributed in precipitates. It has been shown that Fe in solid solution oxidizes closer to the metal-oxide interface than does Fe in precipitates [2]. Since about the same amount of Fe is in solid solution for both alloys, but Zircaloy-4 has much more additional Fe in

SPPs, the contribution of the signal from the Fe in solid solution is much higher for Zr-2.5Nb. Setting aside the difference in how close to the interface the Fe is oxidized, the same behaviors are observed in Zr-2.5Nb samples at higher temperatures (in steam) as those for Zircaloy-4, suggesting a similar mechanism of oxidation of Fe in the oxide.

Nb XANES

Nb XANES spectra were also acquired for each of the three Zr-2.5Nb samples. One goal was to compare the differences between the oxidation of Fe and Nb in the oxide layer. Fig. 4 shows the raw Nb spectra for the oxide layers formed in these three Zr-2.5Nb samples, where again light blue is the metal and dark blue is the oxide.

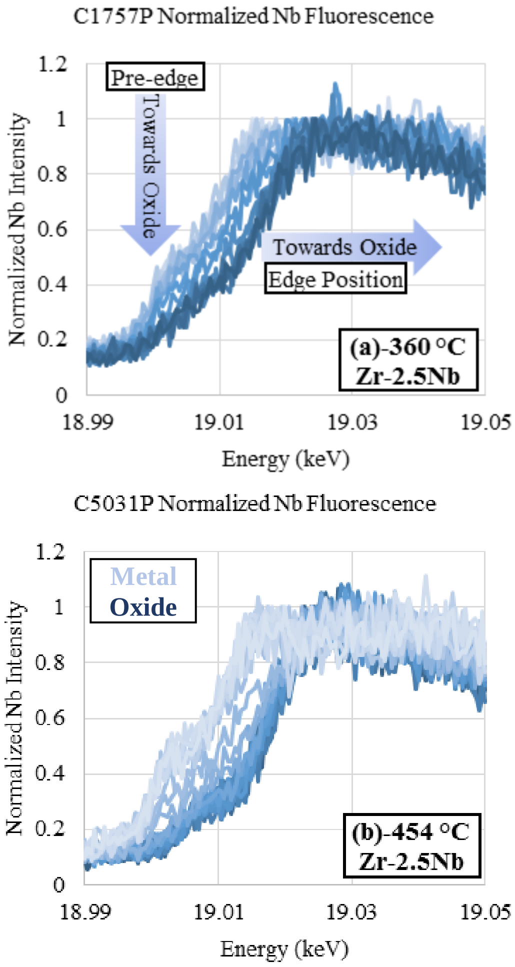

Fig. 4. (a)-(b) Examples of normalized Nb fluorescence from Zr-2.5Nb samples corroded at two different temperatures (360 °C and 454 °C)

Similar to Fig.1, the shift in the spectra is consistent with what would be expected as a greater portion of the signal is generated from oxidized Nb deeper into the oxide layer. Fig. 5 shows the metallic fraction of Nb as a function of distance from the metal-oxide interface for these three Zr-2.5Nb samples from the results of the fitting of the Nb fluorescence spectra to spectra from Nb standards.

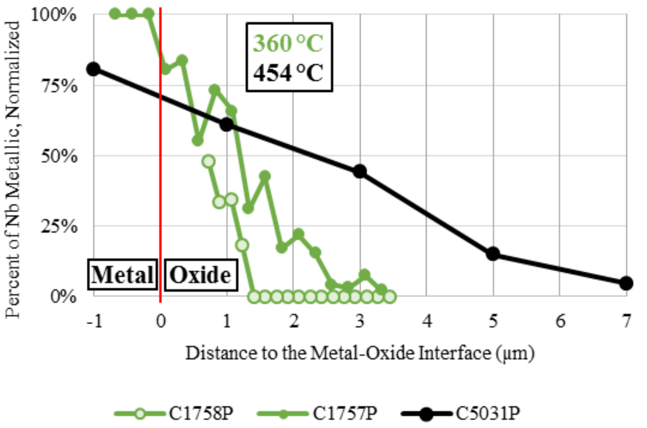

Fig. 5. Combined plot showing the percentage of metallic Nb as a function of distance from the metal-oxide interface for Zr-2.5Nb samples (360 °C in green, and 454 °C in black)

Fig. 5 shows that the percentage of metallic Nb reaches zero between 0.7-1.2 µm in the layer formed during corrosion at 360 °C and reaches zero in the 2-3 µm range at 454 °C, in line with the data from Fe XANES measurements. Here also the alloying elements remain metallic in the oxide layer for a longer distance in the oxide layers formed at higher temperature than for the samples formed at lower corrosion temperatures. Fig. 6 shows a comparison between the oxidation of Fe and Nb in Zr-2.5Nb as determined from XANES scans of all three samples.

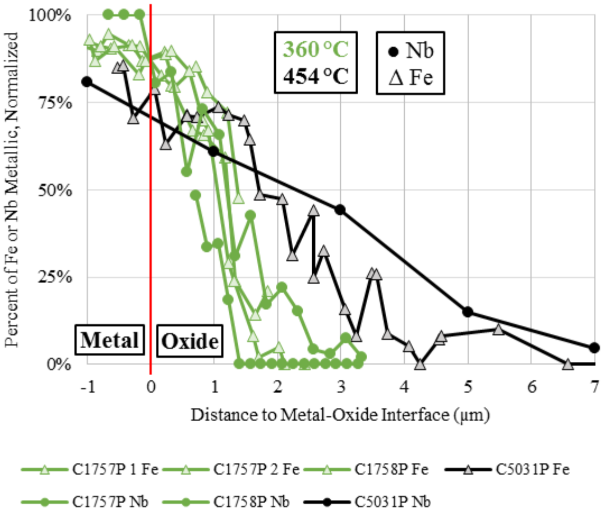

Fig. 6. Comparison of the percentage of metallic Fe or Nb as a function of distance from the metal-oxide interface for Zr-2.5Nb samples (360 °C in green, and 454 °C in black)

Noteworthy is the similarity between the oxidation of Fe and Nb, which appear to oxidize at approximately the same distance from the metal-oxide interface, suggesting that the oxidation of these elements in Zr-2.5Nb is similar. This is consistent with previous comparisons of oxidation states of Fe and Nb in ZIRLO® [2]. A more detailed study would be needed to determine any smaller differences between the oxidation of Fe and Nb in regards to preferential oxidation of βNb or $Zr(Nb,Fe)_2$ precipitates. This data shows that in Zr-2.5Nb, Nb and Fe (which are both incorporated in the Zr matrix mostly in precipitates) oxidize at approximately the same distance from the metal-oxide interface and an increase in temperature causes the Fe and Nb to maintain a more metallic character at a greater distance from the metal-oxide interface.

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