

Corrosion-related defects in Zircalloys: a preliminary study with slow positron beam

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Abstract. Corrosion-related microstructure and defects in Zircaloy-4 and N18 alloys were investigated by variable energy positron annihilation spectroscopy. The specimens were corroded in 0.01mol/L LiOH aqueous solution at 360 °C/18.6 MPa and in super heated steam at 400 °C/10.3 MPa, respectively. Defect profiles were analyzed by measuring the *S* parameter as a function of incident positron energy from 0.25 to 27 keV. Results indicated that Zircalloys corroded in LiOH aqueous solution contained more defects in the oxide layer than that in superheated steam, which implies that formation of defects in oxide layer may relate to the effects of Li⁺ ions in corrosion solution.

Introduction

Zirconium based alloy (Zircaloy) has been widely used as cladding materials in nuclear reactors due to its low thermal neutron capture cross section, good corrosion resistance and adequate mechanical properties [1]. During its service in reactors, Zircaloy was corroded in high temperature high pressure condition. Corrosion-induced defects of Zircaloy are one of the important degradation phenomena in long term operation in nuclear reactors. Research indicated that the corrosion process led to a volumetric expansion of the oxide layer as zirconium (Zr) near the oxide-metal interface region were oxidized and transformed to zirconia (ZrO₂). It is widely known that high compressive stresses were built up during oxidation due to a high Pilling-Bedworth ratio (1.56 for Zr). Under these high compressive stresses, the dense oxide was formed near the interface which controlled the corrosion behavior of Zircalloys. However, the relaxation of the stress in companion with the destabilization might happen while the oxides were formed, which led to defects in the oxide layer [2, 3, 4]. Analyzing the details of these defects will contribute to the understanding of the corrosion mechanism of Zircalloys. Positron annihilation spectroscopy (PAS) has been widely used as a probe for defect studies at the atomic dimension in solids, such as vacancies, vacancy clusters, dislocations, and nanometer-scale voids. The use of variable energy positron beams allows one to probe the depth profile of solids, and is particularly suitable for analysis of surface and near-surface defects [5]. In this work, corrosion-related microstructure and defects in Zircaloy-4 and N18 alloys in 0.01mol/L LiOH aqueous solution at 360 °C/18.6 MPa and in super heated steam at 400 °C/10.3 MPa were investigated by slow positron beam-based Doppler broadening spectroscopy.



Experiment

Specimens with 20mm × 10mm × 1.0 mm in size were cut from Zircaloy-4 (denoted as Zr-4) and N18 alloy plates for corrosion tests and Doppler broadening measurements. Chemical composition of both alloys is shown in table 1. One group of specimens was corroded in an autoclave with 0.01 mol/L LiOH aqueous solution at 360 °C/18.6 MPa for 30 days (denoted as Zr-4-360 and N18-360, respectively), while another group of specimens was corroded in super heated steam at 400 °C/10.3 MPa for 30 days (denoted as Zr-4-400-s and N18-400-s). The thicknesses of the oxide layer induced by corrosion were about 1~2 μm, which were estimated by measuring the weight gain of these specimens before and after the corrosion tests. Prior to the corrosion test, the specimens were annealed at 580 °C for 4h in a vacuum furnace at about 5×10^{-3} Pa, and cleaned using a pickling solution (a mixture of 10 vol.% HF, 30 vol.% HNO₃, 30 vol.% H₂SO₄ and 30 vol.% H₂O), sequentially rinsed in cold tap water, boiling deionized water and then blow-dried with warm air.

Table 1: Chemical composition of Zr-4 and N18 alloys (wt.%).

| | Sn | Fe | Cr | Nb | Zr |
|------|-----|-----|-----|------|----------|
| Zr-4 | 1.5 | 0.2 | 0.1 | — | Balanced |
| N18 | 1.0 | 0.3 | 0.1 | 0.35 | Balanced |

Doppler broadening measurements of uncorroded and corroded specimens were carried out by the slow positron beam with incident positron energies E from 0.25 to 27 keV, and a high purity-Ge detector with an energy resolution of 1.64 keV at 511keV peak was used to collect the annihilation γ energy spectra. 10^6 annihilation events with a count rate of 1000 cps near the 511 peak were collected in each Doppler broadening spectrum.

Results and Discussion

Figure 1 shows S parameter as a function of incident positron energy in uncorroded and corroded specimens. The S - E curves show that there exists a peak value of S parameters in uncorroded Zr-4 and N18 specimens when positron incident energy is from 0.25 to around 8 keV, which indicates an interface defect layer near the oxide-metal interface region. Then with further increasing positron incident energy, the S parameters tend to a plateau where most positrons are implanted in the Zr substrate and annihilate therein.

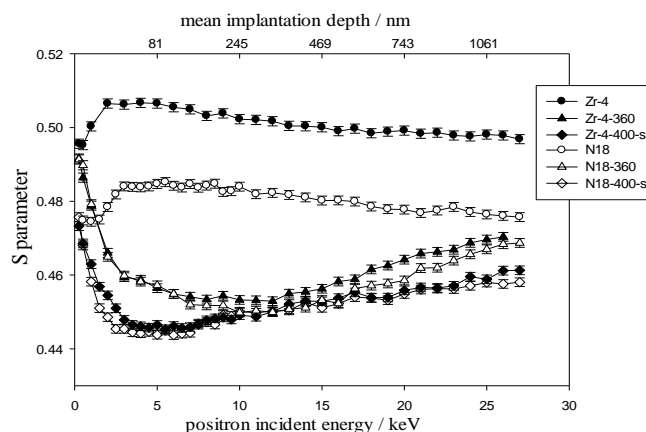


Figure 1. S parameter as a function of incident positron energy in uncorroded and corroded specimens.

The S - E curves of uncorroded Zr-4 and N18 specimens from figure 1 were fitted by VEPFIT using a two-state model (interfacial defect layer and substrate or bulk). Table 2 shows fitted values of S parameter, positron diffusion length in the interface layer and in the Zr substrate, and the thickness of interface layer. In uncorroded Zircalloys, defects were mainly located in the oxide-metal interface layer

with thickness of 100~150 nm. In addition, the S parameter in Zr-4 substrate is larger than that in N18 substrate. This is due to Nb element in N18 alloy whose outer electronic configurations are $4d^45s^1$, which gives positron more chances to annihilate with high-momentum electrons, leading to a smaller S value.

Table 2: Fitted S values of the diffusion length in interface layer (L_d) and in the Zr substrate (L_B), S parameter in interface layer (S_d) and in the Zr substrate (S_B), and thickness of interface layer (B_d).

| | S_d | L_d (nm) | B_d (nm) | S_B | L_B (nm) | Chi-square |
|------------|--------------------|-------------|-------------|--------------------|-------------|------------|
| Zr-4 | 0.5078 ± 0.023 | 10 ± 2 | 112 ± 8 | 0.4996 ± 0.012 | 103 ± 6 | 32 |
| N18 | 0.4842 ± 0.034 | 11 ± 2 | 148 ± 9 | 0.4798 ± 0.017 | 105 ± 9 | 42 |
| Zr-4-360 | 0.4552 ± 0.025 | 115 ± 8 | — | — | — | 45 |
| N18-360 | 0.4523 ± 0.032 | 118 ± 8 | — | — | — | 48 |
| Zr-4-400-s | 0.4463 ± 0.026 | 76 ± 5 | — | — | — | 34 |
| N18-400-s | 0.4435 ± 0.037 | 73 ± 6 | — | — | — | 36 |

The S - E profiles of corroded specimens shown in figure 1 are evidently different from those of the uncorroded ones. The S parameters of Zr-4-360, Zr-4-400-s, N18-360, N18-400-s specimens decrease rapidly as the positron incident energies increasing from 0.25 to 3 keV, then keep unchanged as the positron incident energies increasing from 3 to 15 keV and finally increase slowly with positron incident energy. For the corroded specimens, S parameters and diffusion lengths of the oxide layer were fitted by VEPFIT using positron incident energy from 0.25 to 15 keV, and the fitted S values and diffusion lengths are also shown in table 2. As most incident positrons were implanted and annihilated in the oxide layer. The smaller S values of corroded specimens are due to the broadened momentum distribution of electrons from the oxygen p state, which can attributed to an origin of the small value of S for ZrO_2 [6].

It is interesting to observe in figure 1 that S parameters of Zr-4-360 and N18-360 are larger than Zr-4-400-s and N18-400-s, which indicates that more defects were induced in the oxide layer when Zircalloys corroded in 0.01 mol/L LiOH aqueous solution at 360 °C/18.6 MPa. This difference is due to the action of Li^+ ions in corrosion aqueous solution. Previous studies showed that when Zircalloys corroded in LiOH aqueous solutions, the Li^+ ions can easily enter the oxide layer. The Li^+ ions could be absorbed by vacancies and holes in the oxide layer and led to a decrease of the surface free energy of vacancies, which would accelerate the procedure of the diffusion of defects and the formation of pores and micro-cracks [7]. Meanwhile, as the radius of Li^+ ions and Zr^{4+} ions are approximately equal (the radius of Li^+ ions are 0.076 nm, the radius of Zr^{4+} ions are 0.072 nm), Zr^{4+} ions can be easily displaced by Li^+ ions and produce an amount of anion vacancies. It is noted here that these vacancies can make O^{2-} enter the oxide layer easier, and accelerate the corrosion rate of Zircalloys [8].

Furthermore, the S parameter of Zr-4-360 is larger than N18-360, which indicates that fewer defects were induced in N18-360 specimen, in agreement with the better corrosion resistance of N18 alloys in LiOH aqueous solution [9]. Besides, there does not exist an evident difference of S - E curves in Zr-4-400-s and N18-400-s specimens, indicating that total defect concentrations in both Zircalloys were similar. However, for specimens corroded in super heated steam for long-term corrosion (475 days, about 20 μ m thickness of oxide layer), positron annihilation lifetime measurements found that defect size of oxide layer in N18 is smaller, but higher concentration of larger-scale defects than that of Zr-4 specimens. Further investigations are in progress and will be reported in the future.

Information about the number of defect types could be revealed by plotting the S parameter as a function of the W parameter (S - W plots). All the data for uncorroded and corroded specimens are shown in figure 2. For uncorroded specimens, each S - W plot shows two positron annihilation states, which are in metal-oxide interface and in Zr substrate. The inflection points represent annihilation of positrons trapped in open-volume defects near the surface oxide-metal interface. However, as shown in figure 2, the S - W plots of Zr-4 and N18 specimens are not in the same straight line from interface to

substrate, which is due to the different chemical composition between two kinds of specimens. For corroded specimens, the S and W values all fall on a common locus, which consists of two straight-line segments connecting three verticals. As E is increased the points move along the bottom segment from right to left and then along the top from left to right. Positrons annihilate from surface to oxide layer as E is increased, and then from oxide layer to interface layer and substrate at higher energy. Positron annihilation states in oxide layer and interface layer are very complicated, further investigations have to be done.

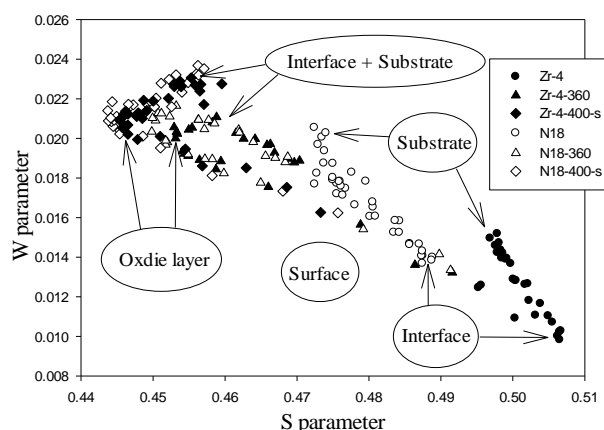


Figure 2. W parameter as a function of the S parameter for uncorroded and corroded Zircalloys.

Conclusions

Slow positron beam Doppler broadening measurements of corroded Zircalloys showed that open-volume defects were induced during the corrosion. When Zircalloys corroded in 0.01 mol/L LiOH aqueous solution at 360 °C/18.6 MPa, more defects were introduced in the oxide layer compared to the corrosion in superheated steam 400 °C/10.3 MPa. This should be the effect of Li^+ ions in the corrosion solution. Furthermore, the S parameter of Zr-4-360 is larger than N18-360 which indicates that fewer defects were induced in N18-360 specimens during the corrosion, in agreement with better corrosion resistance of N18 alloys in LiOH aqueous solution.

Acknowledgments

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