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**Deuterium Absorption in CANDU<sup>®</sup> Zr-2.5Nb  
Pressure Tubes**

**Absorption de deutérium dans les tubes de force  
Zr-2.5 Nb des réacteurs CANDU<sup>MD</sup>**

R.A. Ploc, G.A. McRae

Paper presented at the "14<sup>th</sup> International Corrosion Congress",  
held in Cape Town, South Africa, 1999 September 26  
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Corrosion and Surface Science Branch  
Chalk River Laboratories  
Chalk River, ON K0J 1J0

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**ABSORPTION DE DEUTÉRIUM DANS LES TUBES DE FORCE Zr-2.5 Nb  
DES RÉACTEURS CANDU<sup>MD</sup>**

par

R.A. Ploc et G.A. McRae

**RÉSUMÉ**

La corrosion des tubes de force Zr-2.5 % Nb des réacteurs CANDU<sup>MD</sup> dans l'eau lourde se traduit par la formation d'une pellicule d'oxyde et par l'absorption de deutérium par l'alliage. S'il est admissible que les concentrations de deutérium dépassent la solubilité à l'état solide finale de l'alliage, les deutérures peuvent se former en limitant par là-même la vie utile d'un composant.

Dans les tubes de force des réacteurs CANDU, les vitesses d'entrée sont en grande partie déterminées par le  $\beta$ -Zr métastable qui est présent sous la forme d'une couche mince enrobant les grains  $\alpha$ -Zr prédominants (environ 90 % par volume). La répartition et la continuité de la phase  $\beta$  corrodée dans l'oxyde fournit une toile étendue pour le développement de la porosité interreliée allant de la surface libre à l'interface de l'oxyde du métal. La modification de la distribution de la phase  $\beta$  dans l'alliage change la nature de la porosité de l'oxyde, technique que l'on peut utiliser pour réduire les vitesses d'entrée de deutérium.

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**ABSTRACT**

Corrosion of CANDU® Zr-2.5%Nb pressure tubes in heavy water results in the formation of an oxide film and the absorption of deuterium by the alloy. If deuterium concentrations are allowed to exceed the terminal solid solubility of the alloy, brittle deuterides can form, thereby limiting the service life of a component.

In CANDU pressure tubes, ingress rates are largely determined by the metastable  $\beta$ -Zr that is present as a thin layer encasing the predominant  $\alpha$ -Zr grains (approximately 90% by volume). The distribution and continuity of the corroded  $\beta$ -phase in the oxide provides a pervasive web for the development of interconnected porosity from the free surface to the oxide/metal interface. Changing the distribution of the  $\beta$ -phase in the alloy changes the nature of the oxide porosity, a technique that can be used to reduce deuterium ingress rates.

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## 1. INTRODUCTION

Oxide films on zirconium grow by the inward diffusion of oxygen<sup>1,2</sup>. Mass profiling<sup>3</sup>, however, has demonstrated that the production of oxygen and deuterium during corrosion in heavy water can occur anywhere between the free surface and the oxide/metal interface. Oxide texture generation and cracking are caused by the large volume expansion of the metal upon oxidation, 1.56 times, unconstrained<sup>4</sup>.

Once a thermal oxide film exceeds a thickness of approximately 250 nm, it continues to grow in a manner that allows for stress relief, developing columnar oxide crystallites with boundaries that are perpendicular to the free surface. Oxidation-induced strain is similar to the deformation of a deck of cards which slip past one another when a force is applied. The boundaries of the oxide columns and pores provide short-circuit diffusion paths for inward-migrating oxygen and deuterium. If oxide pores are connected to the free surface, they will provide a means for the aqueous medium to reach the oxide/metal interface, reducing diffusion path lengths and the protective nature of the oxide film. Water reduction within the oxide film can concentrate lithium within pores (CANDU<sup>®</sup> water chemistry uses Li to control the pD<sub>RT</sub>), raising the local pD (pH in light water) and accelerating localized corrosion rates. A high-pD, high-temperature aqueous environment can also cause dissolution of the oxide<sup>5</sup>, which can interconnect adjacent pores.

Deuterium absorption in Zr-2.5Nb is an important concern, because it can limit the service life of a component due to possible formation of brittle deuterides. It is well known that single-phase zirconium alloys (in particular, the Zircaloy) incorporate a high percentage (>80%) of the hydrogen released by the corrosion process. In two-phase alloys, such as Zr-2.5Nb, hydrogen absorption is about an order of magnitude less (<10%). Zr-2.5Nb is composed of  $\alpha$ -Zr (approximately 90% by volume, containing 1% Nb) and metastable  $\beta$ -Zr (containing about 20% Nb). The oxide microstructures that form from these phases are not identical, an important difference being that the corroded  $\beta$ -Zr contains a relatively high concentration of Nb. It has been suggested that the low ingress rates in Zr-2.5Nb are due to Nb<sup>6</sup>. In an oxide film, Nb on a pore surface is likely present as Nb<sup>+5</sup> (i.e., Nb<sub>2</sub>O<sub>5</sub>), since it exists in a relatively high oxygen partial-pressure environment (compared to inside the bulk oxide). It has been speculated that the local excess positive charge (Nb<sup>+5</sup> vs Zr<sup>+4</sup>) retards deuterium absorption, forcing preferential recombination. The amount of Nb<sup>+5</sup> would be minuscule (lining the pores), but has a profound effect on ingress.

For hydrogen to enter the metal it must pass through the oxide film, and for this reason a study of oxide microstructures, in cross-section (from the free surface to the oxide/metal interface), should be instructive when combined with a study of relative hydrogen ingress rates. It is our thesis that the metastable  $\beta$ -Zr distribution in Zr-2.5Nb is key to understanding deuterium ingress rates. Impurities or thermomechanical modifications to the base alloy are expected to modify significantly the nature of the  $\beta$ -Zr, and therefore to modify deuterium absorption rates. That the oxide porosity reported here was developed in situ and not as the result of handling or specimen preparation was demonstrated in a previous publication<sup>7</sup>.

## 2. EXPERIMENTAL

Slices of metal and oxide were cut from several pressure-tube materials and thinned to electron transparency to permit viewing in an analytical electron microscope (AEM), from the free surface to the oxide/metal interface. Residual impurities in the base alloy, such as carbon, can significantly affect deuterium ingress rates; however, in this study, knowledge of the various impurity spectra is not considered to be important, since impurities are believed to be secondary in their effect on the basic mechanism of ingress, which is proposed to be via oxide porosity. It is important to be familiar with the pressure-tube microstructure as shown in Figure 1.

Pressure-tube extrusion flattens and elongates the  $\alpha$ -Zr grains, which develop aspect ratios of about 50/1 in the transverse direction and about 10/1 in the longitudinal. The predominant  $\alpha$ -Zr grains are encased in  $\beta$ -Zr which, therefore, has a three-dimensional structure, pervading the whole metal volume. The same spatial distribution is transferred to the oxide film. In oxide cross-sections the corroded  $\beta$ -Zr appears as thin filaments parallel to the free surface. The filamentary appearance is an illusion resulting from the extreme thinness and orientation of the cross-sections. The true corroded  $\beta$  distribution is a three-dimensional web. Cross-sections can best be thought of as single CAT-scan sections which can, in principle, be computer assembled into a three-dimensional image.

Electrochemical impedance spectroscopy (EIS) was also used to characterize oxide morphology and porosity. The impedance to a low-voltage alternating potential across the oxide was measured as a function of frequency (1 mHz to 100 kHz), and modeled with an electric circuit comprising three generalized Debye elements (constant-phase element, which is a generalized capacitor, and resistor in series) connected in parallel. In practice, only three Debye elements are required to account for the shape of the EIS spectra and hence to characterize the oxide film. The high-frequency element can be related to the large-scale properties of the film and, for example, the overall film thickness can be calculated from the determined capacitance. The other two elements change slowly with time in solution, and are therefore associated with water ingress into two types of porosity: large and small. The small porosity is inferred for the low-frequency response, because it has a much larger series resistance, which is expected for narrower structures. The quality of the regressions of the mid- and low-frequency spectra to the two Debye elements in the model suggests that, from an EIS perspective, two distinct types of porosity are present in the oxide film, as also noted by TEM<sup>7</sup>.

## 3. RESULTS AND DISCUSSION

### 3.1 Electron Microscopy of Oxide Cross-sections

Fresnel imaging was used to examine oxide cross-sections in the TEM. By slightly over- and under-focusing the electron image, black and white fringes appear around the pores. At exact focus, the pores are extremely difficult to detect, because their visibility depends on differences in absorption contrast, which is very weak when the differences in foil thickness are modified only slightly by the presence of a pore.



Figure 1. Typical pressure-tube microstructure, looking at the longitudinal/transverse plane, showing the predominant  $\alpha$ -Zr flattened grain structure surrounded by smaller amounts of  $\beta$ -Zr (gray areas).

Figure 2 shows a typical oxide cross-section. Two types of porosity are visible: large at L and fine at F. The film contains columnar crystallites from 25 to 100 nm in width and several times as long. Since cross-sections taken from orientations that lie in the plane of the current micrograph and parallel to the free surface yield similar images, it can be concluded that the columnar crystallites are equiaxed in cross-section. Bending and other distortions in the oxide crystallites, as well as crystallite overlap, make identification of their boundaries difficult. Small changes in the relative orientation of the electron beam and the oxide foil cause large changes in the crystallite appearance. Finely spaced fringes arise from multiple diffraction through overlapping crystallites.

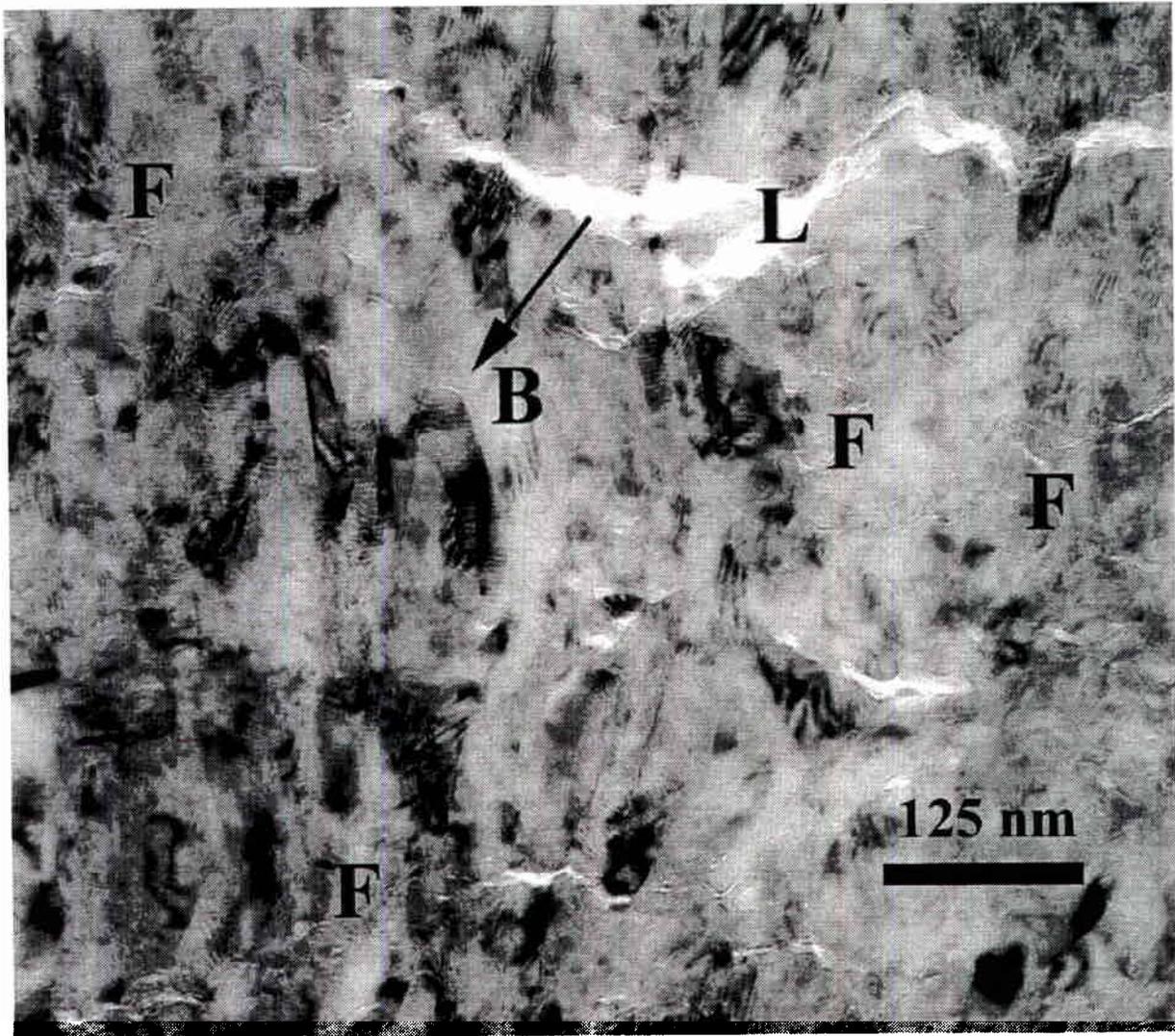


Figure 2. Oxide cross-section showing two predominant forms of porosity: large (channel porosity) at L and fine at F. At B, the fine porosity can be seen to follow the oxide column boundaries.

At B in Figure 2, fine porosity follows the column boundary. In areas such as that indicated by the arrow, it also caps the oxide columns. By tilting the oxide foil in the electron microscope, the three-dimensional nature of the porosity can be partially deduced. The complete pore distribution and shape cannot be fully appreciated using the micrographs shown here, since pores that form on boundaries coplanar with the foil surfaces are invisible. Hence, there is an illusion that pores are narrow and circular in cross-section.

Fine porosity gives the appearance of small-diameter tubes, because they are invariably seen edge-on. Tilting hints at the true shape, which is flake-like (essentially, two-dimensional). Flakes probably result from sliding of the oxide columns caused by the stresses generated during oxidation, in much the same way that planar porosity results when two wet panes of glass are forced apart. With tilting, it can be shown that the large porosity can be best described as ribbon- or channel-like. Only short segments of the channels are seen in any micrograph, because the channels are convoluted, twisting and plunging throughout the oxide bulk (and out of the foil). The microscopy of pore characterization has been more fully reported elsewhere<sup>8</sup>.

The microstructures of  $\beta$ - and  $\alpha$ -Zr oxides are different. Since porosity forms along the top and bottom of columns, a string of pores is developed colinear with, and at, the corroded  $\alpha/\beta$  boundaries. Oxidation stress and dissolution by the high-temperature, high-pD heavy water joins the pores much like opening a zipper. Figure 3 shows pores on both sides of a corroded  $\beta$ -ligament (confirmed by Nb X-ray analysis). The oxide free surface is about 200 nm above this ligament.  $\beta$ -Zr is the web upon which channel porosity develops to produce an interconnected path from the free surface to the oxide/metal interface.

On any given micrograph, only parts of the pore channel will be seen, because it follows the three-dimensional convolutions of the  $\beta$ -web (the foil is essentially two-dimensional). In some instances, the channels are interconnected in the vertical direction (perpendicular to the free surface) through dissolution of oxide bridges between flake pores. It follows, then, that if channel porosity is primarily responsible for deuterium absorption by allowing the corroding medium to enter deeply into the oxide bulk, changing the  $\beta$ -Zr distribution in the metal will have an affect on the rate of deuterium uptake. Indeed, mechanical treatments such as shot-peening destroy the organized second-phase distribution and the deuterium uptake rate drops by a factor of two or three<sup>9</sup>. Figure 4 shows a cross-section of an oxide grown on shot-peened Zr-2.5Nb. Note the predominant flake structure of the pores, the lack of interconnectivity and channel porosity. The large vertical cracks were likely generated by the large oxidation stresses, and are not as numerous as this micrograph suggests. The first micrometer of this oxide (the outer region) was formed in 673 K steam for 24 h, and hence its different appearance. Columnar oxide is visible near the oxide/metal interface.

As stated in the introduction, Zr-2.5Nb has a low deuterium pickup rate compared to other Zr alloys. The reason for this is speculated to be that the channel porosity, which is responsible for determining ingress rates, forms at the corroded  $\alpha/\beta$  boundaries, where there is a high concentration of Nb. The surplus positive charge ( $\text{Nb}^{+5}$  compared to the  $\text{Zr}^{+4}$ ) lining the pore walls means that the positively charged deuterons are less prone to be absorbed onto the pore surfaces. Deuterons, unlike atoms, are always associated with an ion, and in this case the oxygen of the oxide. The decreased propensity for absorption onto the pore walls, combined with the

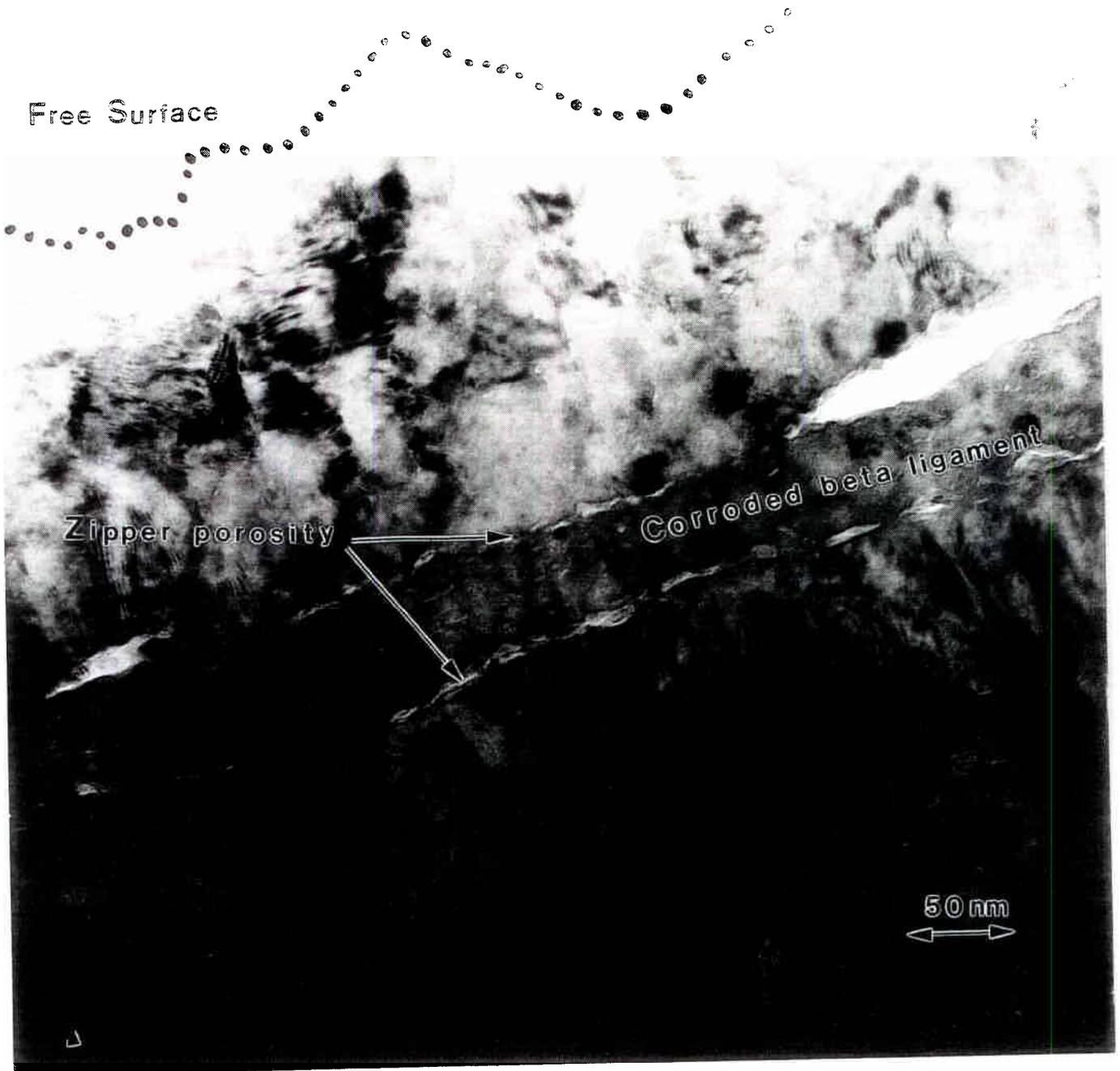


Figure 3. Porosity along the corroded  $\alpha/\beta$ -Zr boundaries. Note how the upper channel is being opened along the line of weakness.

multivalency of the Nb, which acts as a cathodic discharge center, means that the probability for recombination of the deuterons is high compared to the same potential for other Zr oxides (Zircalloys); hence, the low pickup rates for Zr-2.5Nb.



Figure 4. Cross-section of oxide grown on shot-peened Zr-2.5Nb. Porosity is predominantly flake type.

### 3.2 Independent EIS Data

Electrochemical impedance spectra of oxide films have been obtained from three pressure tubes removed from CANDU reactors. Multiple spectra were measured for each tube at slightly different locations to account, at least partially, for variability. In each instance, the spectra could be fitted adequately with the model of three Debye elements connected in parallel. A typical spectrum is shown in Figure 5.

If the oxide film could be modeled after a standard RC series circuit at high frequency, where the impedance of a capacitor ( $\sim 1/\text{frequency}$ ) is small, the circuit impedance would be mainly due to the resistor and the phase angle would be close to zero. As the frequency is lowered, the impedance of the capacitor increases and the phase angle approaches  $-90^\circ$ . In the oxides studied here, as the frequency is lowered the impedance of the high-frequency capacitor becomes so large that current is shunted to the lower impedance path of the second Debye circuit, which has been associated with large porosity. The phase angle is then increased, because the impedance of the second Debye capacitance is low relative to its series resistance. Ultimately, as the frequency is lowered even further, the impedance of this capacitor overtakes that of its series resistor and the phase angle again approaches  $-90^\circ$ , where it would stay were it not for the third Debye element shunting off current at even lower frequency and pulling the phase angle up. In this way, the number of parallel Debye circuits required to account for the data can be determined from an analysis of the deviations of the phase-angle plots.

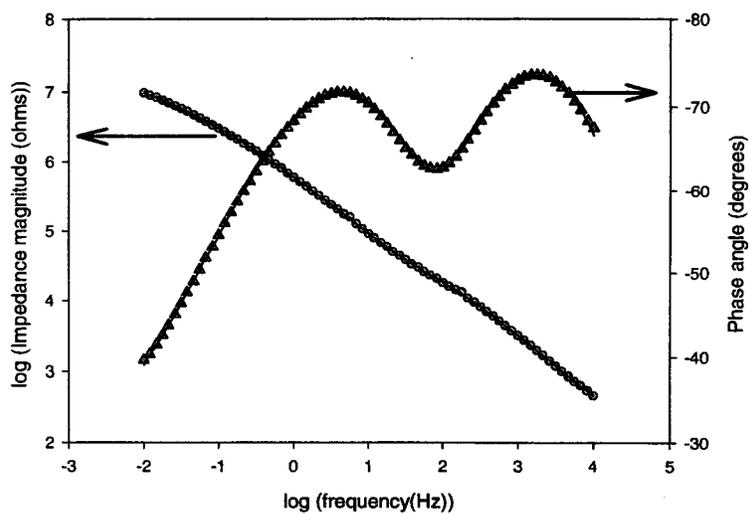


Figure 5. Measured impedance magnitude (circles) and phase angle (triangles) for a removed pressure tube (the horizontal arrows connect the plots with the appropriate axes). The curves through the data are derived from the best-fit parallel Debye model.

Correlations were calculated between the determined parallel-Debye model parameters and the deuterium concentrations from adjacent regions that were sampled and analyzed by hot vacuum extraction mass spectroscopy. No correlations were found between deuterium ingress and any of the parameters of the high-frequency response. The implication is that the thickness of the dense oxide layer is not directly related to deuterium ingress.

There is evidence for correlations between ingress and parameters of the lower frequency responses. The most intriguing is that found with the fractal dimension of the large porosity shown in Figure 6. In essence, a smaller fractal dimension means that the large pores are less sinuous and convoluted. The negative correlation would be consistent with the observations of large-scale zipper porosity in TEM cross-sections of pressure tubes with high deuterium concentrations. The correlation is probably better than it might appear to be in Figure 6, because in many of the low-ingress tubes there was very little evidence for large porosity in the impedance spectra.

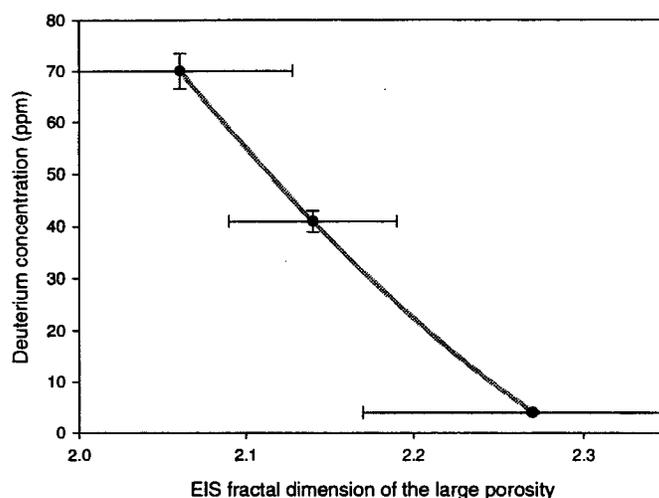


Figure 6. Possible correlation between deuterium ingress and the fractal dimension of the large-scale porosity (impedance spectra analyzed assuming parallel Debye responses).

#### 4. CONCLUSIONS

Two types of porosity exist in aqueous-formed oxide films on Zr-2.5Nb: flake and channel. Channel porosity is the primary route for deuterium ingress into the base alloy. It forms along corroded  $\alpha/\beta$ -Zr boundaries, and these provide the continuous web that steers the channel porosity from the free surface to the oxide/metal interface. An independent technique of measuring the impedance of the oxide films has demonstrated that channel porosity can be correlated with deuterium ingress in pressure tubes from a CANDU power reactor. Disrupting the continuity of the  $\beta$ -Zr phase disrupts the deuterium ingress rate. Any thermomechanical technique that modifies the  $\beta$ -Zr phase can be used to reduce the deuterium ingress rates. Reduced deuterium ingress rates in Zr-2.5Nb, compared to other low-addition Zr alloys, are due to the presence of Nb lining the walls of the channel porosity.

#### 5. ACKNOWLEDGEMENTS

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