ELECTROMAGNETIC EVALUATION OF THE CONCENTRATION OF HYDROGEN DIFFUSED IN ZIRCONIUM ALLOYS USED IN PHWR

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Abstract. In this paper we propose the nondestructive determination of the deuterium content from the pressure tubes using a classical eddy current multi frequency method. The conductivity of the zirconium alloy is determined by inversion, the influence of ZrO layer being eliminated. The developed model, the inversion method and the comparing of prediction - experiment are presented, the data obtained experimentally validating the proposed method.

Introduction

Pressurized Heavy Water Reactors (PHWR), contains an horizontal cylindrical vessel, named Calandria vessel, filled with D_2O used as neutrons moderator. The normal temperature of the moderator is 70^0C. The ends of the vessel have holes in which fuel channels are inserted. The number of fuel channels depends on the power developed by the reactor. In the case of PHWR CANDU type [1], for 600MWe are used 380 fuel channels.

One channel fuel is made from two concentrically tubes, the internal one with 6.3m length, 105mm inner diameter and 4.15mm wall thickness is called pressure tube and is made from Zr 2.5%Nb. Inside this tube, the fuel channels are inserted and between them D_2O circulates as coolant fluid with the maximum temperature of 270^0C. the external tube is named Calandria tube and is made from Zircalloy 2. Annular space between tubes is filled with N_2 or dried CO_2, under pressure.

The concentricity of the tubes is assured by 4 garter springs. During the operation of reactor, two mechanisms of hydrogen (deuterium) apparition are possible [2].

a) hydrolysis of heavy water $2D_2O \rightarrow 2D_2 + O_2$, deuterium appeared may diffuse in the pressure tube's wall from the "hot" internal surface (270^0C) to the "cold" (~100^0C) external

b) corrosion of Zr 2.5%Nb alloy $D_2O \rightarrow ZrO + D_2$,deuterium developed may also diffuses.

Due to the hydrogen diffusion, if the hydrogen concentration exceeds a certain threshold [3], the hydrogen combines with Zr, resulting zirconium hydrides.

$$Zr + D_2 \rightarrow ZrD_2$$

For small concentrations of Zr hydrides, their orientation is after the pressure tube's circumferential direction. If it exceed a certain threshold of Zr hydrides volume concentration, these will reorient, those with radial orientation being predominant [3]. The existence of these phenomena can lead to the apparition of blisters on the external surface of pressure tubes as well as apparition of the hydrogen delayed cracking. This imposes that the concentration of hydrogen and hydrides should be known as precisely as possible during the functioning of the reactor.

Nowadays, the determination of the quantity of hydrogen diffused as well as the concentration of hydrides is made by destructive methods, cropping samples of material from zones especially chosen by the producer of the reactor [4], [5], with the occasion of nondestructive examination of pressure tubes. This procedure, used in present at the inspection of all CANDU reactors, presents two important disadvantages:

- the method imposes the handling of radioactive substances that must be investigated through different procedures (differential scanning calorimetry, mass spectrometry etc.)

- the hydrogen (deuterium) concentration is determined only in one point of the pressure tube, this being placed on the external surface of calandria vessel, into a zone covered by end-fitting, the results being extrapolated for the entire tube.

During the period 2000-2006, the International Atomic Energy Agency, Vienna has initiated a research program with the aim of finding the best methods for detection and evaluation of discontinuities, blisters and hydrogen content on pressure tubes [6].

For determination of hydrogen content from Zr 2.5%Nb alloys, two methods have been proposed:

- ultrasound method, based on the determination of propagation speed of transversal and longitudinal waves, on determination of the attenuation and ultrasound spectroscopy [7]
- electromagnetic methods [6] that determine the conductivity of Zr alloys with different quantities of absorbed hydrogen, the correlation between the electrical conductivity and hydrogen concentration being experimentally established.

In this paper we present an electromagnetic method for determination of the Zr 2.5%Nb alloy conductivity, presenting the way of solving the forward problem, the linearization and inversion procedures, and the experimental data.

The forward problem

For a circular eddy current coil with rectangular cross-section, closed-form solutions for impedance are given in [8], [9], [10].

The ohmic resistance of the coil will be neglected, the apparition of a real term in the expression of the impedance being due to the presence of a conductive material.

The impedance of the coil, in air, Z_{air} is given by [8]

$$Z_{air} = \frac{2\pi j\omega\mu_0 \mu n^2}{l^2\left(r_0 - r_i\right)^2}\int_0^{\infty}\frac{I^2\left(kr_0, kr_i\right)}{k^5}\left(1+\frac{e^{-kl}-1}{k}\right)dk \qquad (1)$$

where $\mu_0=4\pi \mathrm{x} 10^{-7}$H/m – the permeability of vacuum, n – the number of coil turns, r_0 – outer radius, r_i – inner radius, l- the length of the coil, $I(a,b)=\int_a^b xJ_1(x)dx$, $J_1(x)$ is the Bessel function of the first kind. I can be calculated using Struve functions [11].

In a point of coordinate (x_0, y_0), at height h over an amagnetic conductive plate (μ_r=1) with H thickness and having local electrical conductivity $\sigma(x_0, y_0)$, the impedance of the same coil will be

$$Z\left(x_0,y_0\right)=\frac{2\pi j\omega\mu_0 n^2}{l^2\left(r_0-r_i\right)^2}\int_0^{\infty}\frac{I^2\left(kr_0,kr_i\right)}{k^5}\cdot\left[2l+\frac{1}{k}\left[2e^{-kl}-2+\left(e^{-2k(l+h)}+e^{-2kh}-2e^{-k(l+2h)}\right)\cdot\right.\right.$$
$$\left.\left.\cdot\left[\frac{\left(\gamma^2\left(x_0,y_0\right)-k^2\right)\left(1-e^{-2\gamma\left(x_0,y_0\right)H}\right)}{\left(\gamma^2\left(x_0,y_0\right)+k^2\right)\left(1-e^{-2\gamma\left(x_0,y_0\right)H}\right)-2k\gamma\left(x_0,y_0\right)\left(1+e^{2\gamma\left(x_0,y_0\right)H}\right)}\right]\right]\right]dk \qquad (2)$$

where $\gamma^2\left(x_0,y_0\right)=k^2-j\omega\mu_0\sigma\left(x_0,y_0\right)$.

The last factor from Eq. (2) is the one that contains the information about the electrical conductivity of the material under testing.

We will develop a linearized relation between the observed impedance modification and the conductivity modification.

We note

$$\theta\left(x_0,y_0,k\right)=\frac{\left(\gamma^2\left(x_0,y_0\right)-k^2\right)\left(1-e^{-2\gamma\left(x_0,y_0\right)H}\right)}{\left(\gamma^2\left(x_0,y_0\right)+k^2\right)\left(1-e^{-2\gamma\left(x_0,y_0\right)H}\right)-2k\gamma\left(x_0,y_0\right)\left(1+e^{2\gamma\left(x_0,y_0\right)H}\right)} \quad (3)$$

The Eq.(3) can be developed into a Taylor series around the value σ^0 that represents the value of electrical conductivity of the considered Zr alloy and which do not contain diffused hydrogen.

$$\theta\left(x_0,y_0,k\right)=\theta^0\left(x_0,y_0,k\right)+\left(\sigma-\sigma_0\right)\left.\frac{\partial\theta\left(x_0,y_0,k\right)}{\partial\sigma}\right|_{\sigma=\sigma_0}+\ldots \quad (4)$$

Introducing Eq. (4) in Eq.(2) we can write formally

$$Z\left(x_0,y_0\right)=Z^0\left(x_0,y_0\right)+\left(\sigma\left(x_0,y_0\right)-\sigma_0\right)\int_0^\infty A(k)\left.\frac{\partial\theta\left(x_0,y_0,k\right)}{\partial\sigma}\right|_{\sigma=\sigma_0}dk+O\left(\sigma-\sigma_0\right)^2 \quad (5)$$

where the kernel A represents the factors from Eq. (2) that contains the conductivity.
Due to the convolution nature of the problem

$$\delta Z(k)=\left(\sigma-\sigma_0\right)\left.\frac{\partial\theta\left(x_0,y_0,k\right)}{\partial\sigma}\right|_{\sigma=\sigma_0} \quad (6)$$

with $\delta Z(k)$ the Fourier transform of the variation of the impedance.

Remark: In order to obtain the linearized expression of the impedance modification due to the modification of conductivity, it is necessary that $\left\|Z-Z^0\right\|\le O\left(\sigma-\sigma_0\right)^\alpha$ for any $\alpha\ge 1/2$. This implies that Eq. (5) can be interpreted as a Frechet derivative.

Proposition: Convolution kernel in the linearized Eq. (5), A(k), is analytic in $\mathbf{R}^1$.

Theorem (Uniqueness of the linearized problem): Given impedance data $\delta Z\left(x_0,y_0\right)$ for all $\left(x_0,y_0\right)$, the linearized inverse problem from Eq. (5) admits a unique conductivity profile $\sigma\left(x_0,y_0\right)-\sigma_0$ in L^2.

Proof: We only need to show that if $\delta Z\left(x_0,y_0\right)=Z\left(x_0,y_0\right)-Z^0\left(x_0,y_0\right)=0$, then the only solution for Eq. (5) is $\frac{\partial\theta}{\partial\sigma}=0$. In the Fourier transform domain, what we must show is that $A(k)\frac{\partial\theta(k)}{\partial\sigma}=0$, then $\frac{\partial\theta(k)}{\partial\sigma}=0$. Suppose that $\frac{\partial\theta\left(x_0,y_0\right)}{\partial\sigma}\neq 0$ and $A(k)\frac{\partial\theta(k)}{\partial\sigma}=0$. It means that A(k) must vanish for the same sets of nonzero measure in the k axis. But this is a contradiction until the analyticity property about *A(k)*. If *A(k)=0* in same set of positive measure then it must vanish everywhere. Therefore, we must conclude that the only way for $A(k)\frac{\partial\theta}{\partial\sigma}=0$ for all *k* is for $\frac{\partial\theta}{\partial\sigma}=0$.

The inverse problem

As matrix, the linearized Eq. (5) can be written as

$$\delta z=U\delta\sigma \quad (7)$$

having as unknown the modification of conductivity $\delta\sigma$.

For inversion, different procedures can be used [12], [13]. Despite the model matrix U is sufficient smooth, the existence of the noise making that the matrix shall be enough ill-conditioned. This fact has imposed a previous regularization using Levenberg-Marquardt procedure, the value of regularization parameter being 10^{-12}. The proper inversion was effectuated using generalized inversion in Moore-Penrose sense.

Studied samples

Coupons from pressure tubes with $28x28x4.18mm^3$ have been taken into study (Figure 1).

Figure 1. The studied samples

Because the zirconium burns in air and the temperature of ignition is relatively small, the samples have been cropped using an electro discharge machine.

The initial hydrogen content was lower than 2ppm (this is the limit of detection)

The hydrogen absorption has been made into a Sieverts device that consists from a quartz tube connected to a high vacuum system and to a hydrogen injection system (99.999% purity). The heat treatments were performed by moving the tube into an instrumented furnace. The temperature was measured with a thermocouple installed inside the hydrogenation chamber, placed few millimeters above the sample. The hydrogen estimated concentrations were calculated from the difference between the initial and final pressures measured at room temperature, assuming ideal gas behavior. The real concentration of hydrogen was determined using the differential scanning calorimetry (DSC) method. The features of the samples are presented in Table 1.

Tabel 1. The features of the studied samples

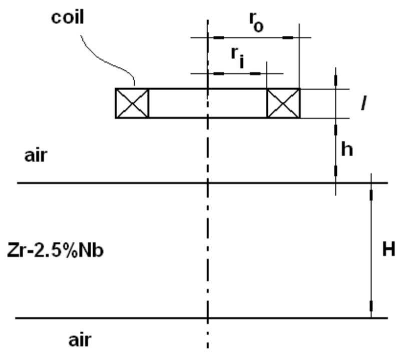
No	Sample	Geometrical dimension $[mm^3]$	Hydrogen [ppm] determined by DSC	Observation
1	01	28x28x4.18	≤2	Serves as etalon -does not exist ZrH_2
2	05	28x28x4.18	≤2	Serves as etalon -does not exist ZrH_2
3	13	28x28x4.18	3	Serves to determine the detection limit
4	06	28x28x4.18	18	ZrH_2 has not been detected
5	07	28x28x4.18	34	ZrH_2 has not been detected
6	18	28x28x4.18	34	ZrH_2 has not been detected - Serves to determine the measurement errors
7	08	28x28x4.18	60	It appears ZrH_2 in low concentration disposed after circumferential direction
8	35	28x28x4.18	87	It appears ZrH_2 in high concentration disposed after circumferential direction, it also appears ZrH_2 disposed after radial direction
9	25	28x28x4.18	87	It appears ZrH_2 in high concentration disposed after circumferential direction, it also appears ZrH_2 disposed after radial direction
10	36	28x28x4.18	89	It appears ZrH_2 in high concentration disposed after circumferential direction, it also appears ZrH_2 disposed after radial direction

The samples were examined by metallographic method, using a classical chemical attack for Zr alloys, to determine the hydrogen concentration from which zirconium hydrides are formed as well as the threshold from which hydrides disposed after radial direction appear.
Using a LakeShare VSM 7410 Vibrating Sample Magnetometer, the relative magnetic permeability has been determined for the samples taken in study as being 1.01±0.005. The samples taken in study are presented in Figure1.

Experimental set-up

The eddy current transducer, one coil type has been connected to a Network/Spectrum/Impedance Analyzer – Agilent 4395A, programmed to effectuate a frequency swap in the range 10kHz - 100kHz, corresponding to a standard skin depth between 3.7mm and 1.2mm for a material with $1.89x10^6$S/m (the conductivity of Zr-2.5%Nb alloy having 3ppm H_2).
The image of the transducer is presented in Figure 2a and the dimensions are given in Figure 2b.
For every frequency used, the memorized results represent the mean of 100 measurements. The self inductance of the measure coil was 892.17μH, the resistance in continuum current was 30.3216Ω. Both measurements have been made with Agilent 4395A at 10Hz frequency, the coil being placed at large distance from any metallic part.
During the measurements, the correction for 1m coaxial cable for connection has been made.

(a) one coil transducer



r_i=4.5mm; r_0=6.5mm; l=2mm, number of turns=100.

(b) geometrical dimensions

Figure 2. The transducer and experimental layout

Experimental Results

The eddy current transducer was placed on the concave side, as well as on the convex side of the examined samples, thus the axis of the transducer coincides with the radial direction of the samples. The following results represent the mean of the resistance and inductive reactance of the transducer for the two positions mentioned above. In each of the positions, 100 measurements have been made.
In Figure 3, we present the dependency normalized inductive reactance ($L\omega / L_0\omega$) by the normalized resistance of the transducer for all examined samples, , in case in which the frequency of the alternative current which circulate through the transducer varies between 10kHz – 100kHz.
Examining the data in the Figure 3, it can be seen that the samples having equal concentrations of hydrogen have perfectly similar behavior, the values of the normalized inductive reactance , as well as of the normalized resistance varying with less than 2%. The extremely detailed analysis of the measurements errors presented in [14] indicates similar values in the case of plane samples.
These measurements have been considered data for the inversion, with a view to determine the electrical conductivity of the Zirconium alloys with different quantities of hydrogen. The inversion has been made for 91 equidistant frequencies within the range 10 kHz – 100 kHz. In order to obtain the fitting of experimental results with the model, given by the equation (1), the procedure indicated in [8] . Due to the fact that in the equation (1) does not exist the possibility of evaluating

the DC resistance of the transducer, from the experimental results has been subtracted the value of the DC resistance, also determined experimentally.
The results of the inversion are presented in Table 2. The dependency of electrical conductivity of Zr-2.5%Nb alloys, obtained by inversion, function of the hydrogen content is presented in Figure 4.

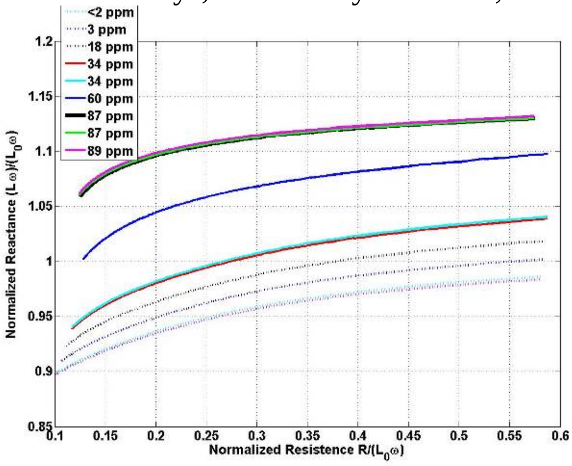


Figure 3. Normalized inductive reactance vs. normalized resistance for examined samples.

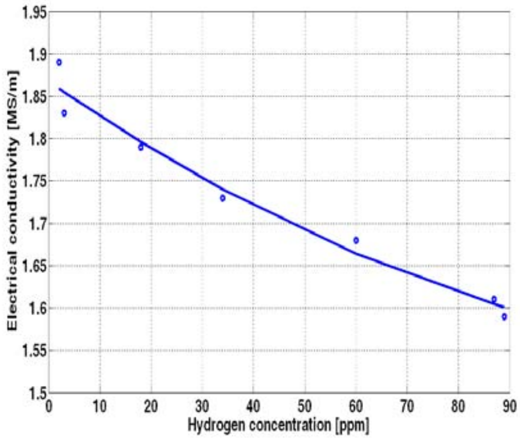


Figure 4. The electrical conductivity v.s. hydrogen concentration

Table 2. Experimental results

No	Sample	Hidrogen content [ppm]	Electrical conductivity [MS/m]	Obs.
1	01	≤ 2	1.89	Value indicated by producer
2	05	≤ 2	1.89	Value due by producer
3	13	3	1.83 ± 0.05	Standard deviation (classical calculated)
4	06	18	1.79 ± 0.05	Standard deviation (classical calculated)
5	07	34	1.73 ± 0.05	Standard deviation (classical calculated)
6	18	34	1.74 ± 0.05	Practically the same value of the sample no. 07
7	08	60	1.68 ± 0.05	-
8	35	87	1.61 ± 0.05	-
9	25	87	1.61 ± 0.05	Rigorous value of the conductivity like in the case of the sample no. 35
10	36	89	1.59 ± 0.05	-

Conclusions

Measuring the modification of the impedance of an eddy current transducer with unique coil , and utilizing a simple inversion procedure starting from a linearized model, it is possible to determine the conductivity of the Zr2.5% alloys used in the fabrication of the pressure tubes from the nuclear PHWR power plants, with different hydrogen contents.

When the electrical conductivity of the alloys exceeds a threshold value of .1.68MS/m, the development of the Zr hydrides oriented after a circumferential direction pressure tubes walls is possible.

If the electrical conductivity exceeds 1.61MS/m, the Zr hydrides start to change orientation after radial direction. In this situation, blisters and hydrogen delayed cracking is possible to appear.

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