

## INVESTIGATION OF THE Zr-2.5%Nb ALLOY STRUCTURE BY ULTRASONIC SPECTRAL ANALYSIS

V. IONESCU, M. MIHALACHE, S. FLOREA

*Institute for Nuclear Research, Pitesti, Romania,*

*E-mail: viorel.ionescu@nuclear.ro*

(Received October 16, 2009)

*Abstract.* The cold-worked Zr-2.5%Nb alloy is used for the pressure tubes in CANDU nuclear reactors. This material has developed a strong texture due to the limited slip system during extrusion process, leading to anisotropic properties. For this reason, it is very important to be able to evaluate its microstructure. In the present paper, we used the ultrasonic scattering properties as a tool for microstructural evaluation of metals.

*Key words:* ultrasonic spectral analysis, ultrasonic attenuation, grain size evaluation.

### 1. INTRODUCTION

The cold-worked Zr-2.5%Nb alloy is used for the pressure tubes of CANDU nuclear reactors. This material has developed a strong texture due to the limited slip system during extrusion process, leading to anisotropic properties. Polycrystalline Zr-2.5%Nb pressure tube is a hexagonal closed packed (hcp) structure and is textured along the circumferential direction. The material properties strongly depend on the orientation distributions and dimensions of grains, which determine a directional anisotropy of elastic stiffness, thermal expansion coefficients, etc.

During the service life in reactor, diffusion of hydrogen and/or deuterium in the pressure tubes wall will occur. Below a certain temperature, a stable hydride will form, as a brittle phase and could lead to catastrophic failure.

The grain size evaluation by ultrasonic methods relies on the ultrasonic velocity and attenuation coefficient measurements. Two mechanisms cause attenuation of ultrasonic waves in solids: scattering and absorption. Scattering attenuation results from the incidence of a wave on boundaries and inhomogeneities in a solid. Absorption of ultrasonic waves occurs during propagation and is caused by the conversion of wave energy to heat. In general, absorption plays a negligible role in the total attenuation of ultrasonic waves in

solids. Attenuation due to scattering in granular materials is determined by the wavelength of propagation,  $\lambda$ , and the characteristic dimension of the inhomogeneity,  $D$ .

When the wave length is very large compared to the grain size ( $\lambda > 2\pi D$ , where  $\lambda$  – wave length,  $D$  - the average grain size), Rayleigh scattering occurs and the attenuation coefficient is given by the theoretical curve[1-3]

$$\alpha = c_1 f + c_4 f^4, \quad (1)$$

where  $\alpha$  is the attenuation coefficient,  $f$  is the frequency of the elastic wave,  $c_1$  is the elastic hysteresis coefficient, and  $c_4$  is the Rayleigh scattering coefficient.

The effect of scattering of high-frequency waves (both shear and longitudinal) due to grains in polycrystalline materials are complex. The effective elastic constants differ from grain to grain.

This difference occurs not only due to random orientation of the grains but also for different grain sizes. Thus, ultrasonic attenuation is a suitable parameter to evaluate the micro-structural configuration of polycrystalline materials. A quantitative knowledge of ultrasonic attenuation in materials gives an idea about the microstructure such as grain size, pore size, etc.

## 2. EXPERIMENTAL PROCEDURE

### 2.1. ATTENUATION MEASUREMENT

When an ultrasonic signal traverses a medium, the frequency components associated with the input signal are altered. To produce the frequency domain information, a discrete Fourier transformation can be used. It is possible to study the effect of material properties on the input signal, by the echo frequency-spectrum analysis.

The frequency dependence of ultrasonic attenuation is determined from the amplitude spectra of two successive back wall echoes from the time domain, deriving from the same emission impulse [4].

In the present paper the ultrasonic attenuation measurements were made at room temperature by the ultrasonic longitudinal waves, pulse-echo contact method. The radio-frequency (RF) signals from the first two back wall surface reflections (E1 and E2 echoes) have been selected and digitized. Each digitized signal was Fourier transformed using an FFT algorithm and were obtained the S1 and S2 spectrums. The frequency dependence of attenuation coefficients,  $\alpha(\omega)$ , is found from the equation [4–6]:

$$\alpha(\omega) = \frac{1}{2d} 20 \lg \frac{A_1(\omega)}{A_2(\omega)}, \quad (2)$$

where  $A_1(\omega)$  and  $A_2(\omega)$  are frequency spectrum amplitudes for S1 and S2 spectrums, and  $d$  is the sample thickness. In the frequency domain the ratio of the amplitudes for a series of frequency components represents the basis for determining a functional relation between the attenuation coefficient and frequency.

The size of the Zr-2.5%Nb alloy particles are in the range of micron dimension, which is much less than the wave length of the ultrasonic wave, so such scattering should belong to Rayleigh scattering regime.

By fitting the experimental data (2) with the theoretical dependence (1), the real coefficients  $c_1$  and  $c_4$  can be experimental determined.

## 2.2. THE GRAIN SIZE EVALUATION

The grain size evaluation using the ultrasonic data is based on the Lifshits and Parkhomovskii theory [1-3]. The attenuation coefficient for hexagonal crystallites in Rayleigh scattering range can be written in the following form:

$$\alpha_s^L = \alpha^{L,L} + \alpha^{L,T} = \frac{\left(\frac{4\pi^3}{450}\right)(Tf^4)}{(\rho_0^2 v_L^3)} \left(\frac{a_1}{v_L^5} + \frac{b_1}{v_T^5}\right) = STf^4, \quad (3)$$

where, have been used the following notations:  $f$  – the ultrasonic wave frequency;  $v_L, v_T$  – the longitudinal and transversal wave velocities;  $T$  – the average grain volume;  $S$  – the proportionality factor

$$S = \frac{\left(\frac{4\pi^3}{450}\right)}{(\rho_0^2 v_L^3)} \left(\frac{a_1}{v_L^5} + \frac{b_1}{v_T^5}\right), \quad (4)$$

where:

$$a_1 = \frac{88}{15}\gamma^2 + 40\chi^2 + 96\eta^2 + \frac{80}{3}\chi\gamma + \frac{128}{3}\gamma\eta + \frac{320}{3}\chi\eta, \quad (5)$$

$$b_1 = \frac{82}{15}\gamma^2 + 30\chi^2 + \frac{272}{3}\eta^2 + 30\chi\gamma + \frac{112}{3}\gamma\eta + 80\chi\eta \quad (6)$$

$$\gamma = C_{11} + C_{33} - 2(C_{13} + 2 C_{44}), \quad (7)$$

$$\chi = C_{13} - C_{12}, \quad (8)$$

$$\eta = C_{44} + (C_{12} - C_{11}) / 2, \quad (9)$$

where  $C_{ij}$  are elastic stiffness.

The relation (3) was written taking into account the mode conversion at scattering process too, for an incident longitudinal wave.

Thus, neglecting the elastic hysteresis loss, for hexagonal crystallites, the average grain volume is obtained from relation:

$$T \approx \frac{c_4}{S}, \quad (10)$$

where  $c_4$  is the Rayleigh scattering coefficient experimental determined.

It is need to correctly determine the anisotropic elastic stiffness. The anisotropy of the Zr-2.5%Nb alloy could be treated as orthorhombic symmetry, consist of three principal coordinates such as radial, circumferential and axial directions. Thus, the elastic stiffness on the tubular sample coordinate could be expressed as an orthorhombic symmetry [7–13].

### 2.3. SPECIMEN PREPARATION

The measurements of acoustic attenuations of Zr-2.5%Nb alloy were performed at room temperature (20°C) using rectangular parallelepiped samples machined from the same tube. The axis of the samples faces are parallel with the axial (A), circumferential (C) and radial (R) directions of the tub.

The measurements have been performed in radial direction. The  $S_0$  sample was in “as received” state and the  $S_1$ ÷ $S_4$  samples were hydrided by slow-rate electrolytic reaction at various concentrations up to aprox. 90ppm. The samples hydrogen content characterization is performed by an ELTRA 04-900 analyser, based on the inert fusion method. The method accuracy is  $\pm 5$  ppm  $H_2$ . It can be seen (Fig. 1) that the slow-rate hydrided samples contain especially  $\delta$  hydrides platelets which form relatively long “filaments” with prevalent orientation in the circumferential direction.

### 2.4. EXPERIMENTAL SYSTEM

The ultrasonic system consists of an analogue ultrasonic pulser-receiver (USIP12/KRAUTKRAMER instrument equipped with the special module DTM12), a longitudinal wave contact transducer (ALPHA HP AEROTECH - 10 MHz /.25 miniature broadband) and a shear wave contact transducer (V156 - 5MHz normal incidence).

For each measured point, the radio-frequency (RF) acquisitioned signals are digitized and processed by spectral analysis software program.

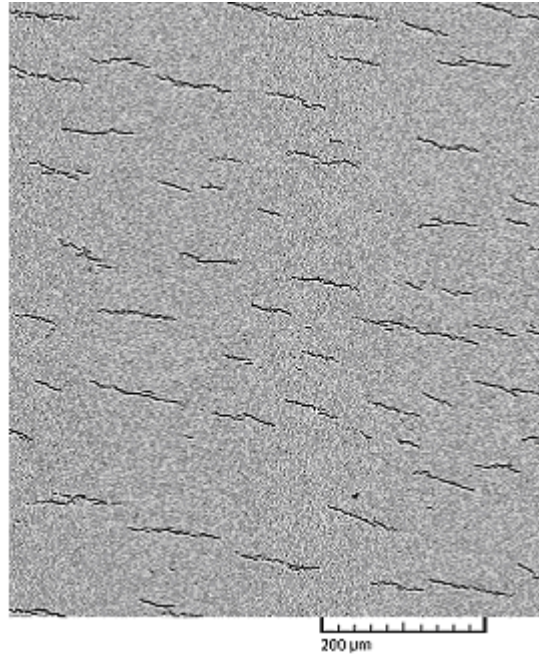


Fig. 1 – SEM image of hydrided Zr-2.5%Nb sample showing the  $\delta$  hydrides trails in radial-circumferential section; hydrogen concentration  $C_H=90$ ppm.

### 3. EXPERIMENTAL RESULTS AND DISCUSSIONS

Firstly, we have performed the longitudinal and transversal ultrasonic phase velocity measurements, on each sample, for the principal tub directions (Table 1). With these data we have determined the Zr-2.5%Nb pressure tube elastic stiffness (Table 2).

Table 1

Longitudinal and transversal ultrasonic phase velocities in Zr-2.5%Nb pressure tube materials.

Sample	$C_H$ [ppm]	$V_L(R)$ [m/s]	$V_T(R)$ [m/s]	$V_L(A)$ [m/s]	$V_T(A)$ [m/s]	$V_L(C)$ [m/s]	$V_T(C)$ [m/s]
S0	10	4688	2272	4675	2266	4788	2349
S1	50	4723	2281	4694	2280	4810	2384
S2	55	4718	2285	4703	2278	4808	2376
S3	65	4738	2287	4692	2281	4808	2377
S4	90	4738	2289	4704	2291	4819	2367

Table 2

Anisotropic elastic stiffness of Zr-2.5%Nb pressure tube materials  
by ultrasonic velocities measurements

Sample	$C_H$ [ppm]	$\rho$ [kg/m <sup>3</sup> ]	$C_{11}$ [N/m <sup>2</sup> ]	$C_{33}$ [N/m <sup>2</sup> ]	$C_{44}$ [N/m <sup>2</sup> ]	$C_{12}$ [N/m <sup>2</sup> ]	$C_{31}$ [N/m <sup>2</sup> ]
S0	10	6480	1.424 E+11	1.486 E+11	3.345 E+10	7.551 E+10	7.530 E+10
S1	50	6480	1.445 E+11	1.499 E+11	3.372 E+10	7.712 E+10	7.704 E+10
S2	55	6480	1.442 E+11	1.498 E+11	3.383 E+10	7.657 E+10	7.569 E+10
S3	65	6480	1.455 E+11	1.498 E+11	3.389 E+10	7.768 E+10	7.730 E+10
S4	90	6480	1.455 E+11	1.505 E+11	3.395 E+10	7.756 E+10	7.743 E+10

Notation of hcp single crystal: 1 = 2 = a-axis, 3 = c-axis.

Notation of sample coordinate system of axes: 1 = Axial Direction, 2 = Radial Direction, 3 = Circumferential Direction.

Next step, we have performed the attenuation measurements. The theoretical curve (Equation 1) of attenuation coefficient is fitted to the experimental data  $\alpha(\omega)$ , by regression analysis, in the considered frequency range (10÷14MHz). Thus, the elastic hysteresis coefficient  $c_1$ , and the Rayleigh scattering coefficient  $c_4$  are determined. The average grain volume was determined from Eq. 10. The obtained data are presented in Table 3.

Table 3

The calculated polynomial coefficients and the average grain volume for Zr-2.5%Nb samples

Sample	$C_H$ [ppm]	$V_L(R)$ [m/s]	$V_T(R)$ [m/s]	$c_1$ [dB/mm Hz]	$c_4$ [dB/mm Hz <sup>4</sup> ]	Grain volume obtained by ultrasonic spectroscopy [ $\mu\text{m}^3$ ]
S0	10	4688	2272	-3.22E-24	9.30E-29	2.96E+3
S1	50	4723	2281	-4.93E-24	2.66E-28	8.86E+3
S2	55	4718	2285	-7.84E-24	2.64E-28	8.89E+3
S3	65	4738	2287	-9.79E-24	3.13E-28	10.9E+3
S4	90	4738	2289	-7.37E-24	3.21E-28	11.0E+3

The variation of attenuation coefficient,  $\alpha$ , with frequency are displayed in Fig. 2.

An other method for average grain size evaluation is the metallographic techniques. The polished samples were etched chemically [14] and investigated by Scanning Electron Microscopy technique. A typical digital microscopy image of Zr-2.5%Nb pressure tube materials is shown in Fig. 3 (for "as received" state), and Fig. 4 (for hydrided state).

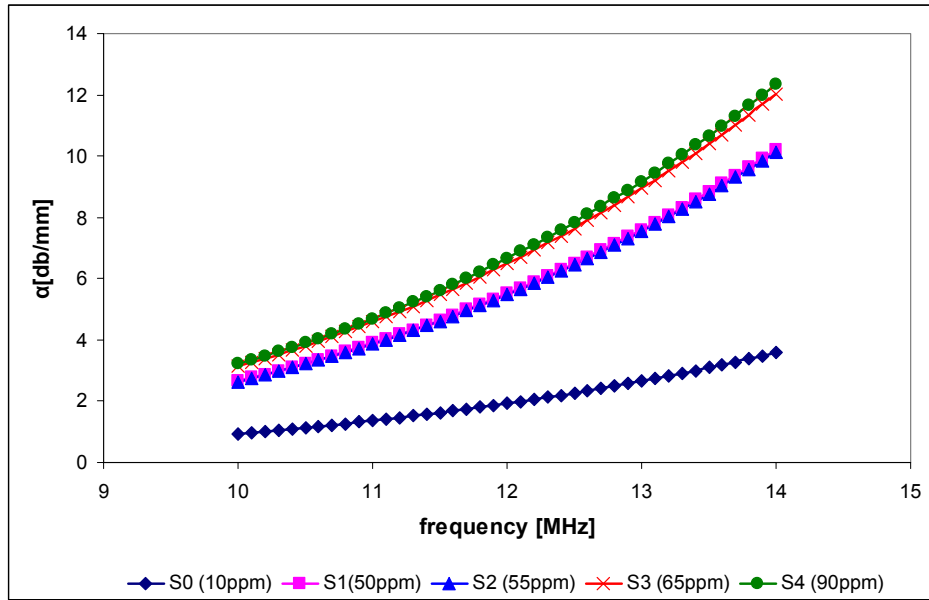


Fig. 2 – The frequency dependence of attenuation coefficients.

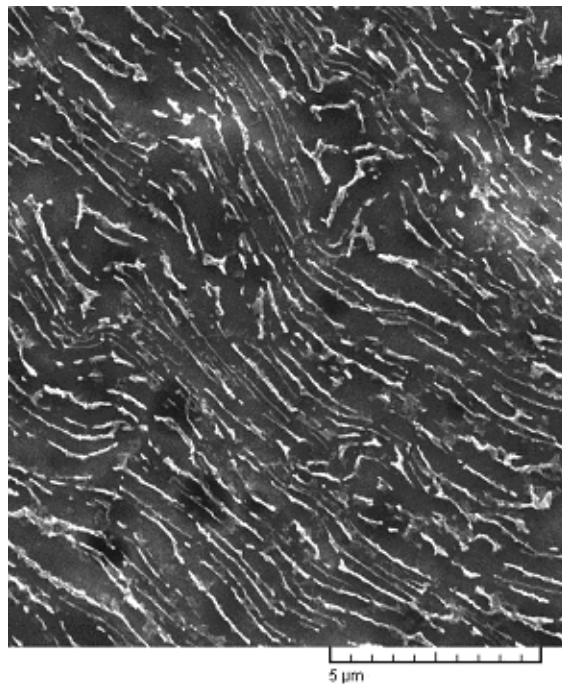


Fig. 3 – SEM image of “as received” Zr-2.5%Nb sample with the grains limits in radial-circumferential section.

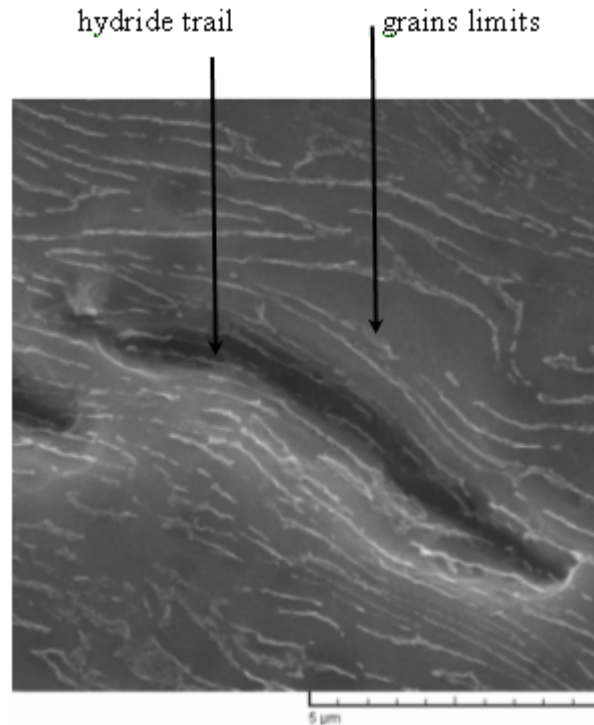


Fig. 4 – SEM image of Zr-2.5%Nb hydrided sample showing the grains limits and hydride trail, in radial-circumferential section.

The grain size evaluation from the planar section was evaluated by chord method, according to ASTM E112. For as received material we obtain the following average values of the grain size: 8–40 $\mu\text{m}$  (in axial direction), 1–10 $\mu\text{m}$  (in circumferential direction) and 0.5–3 $\mu\text{m}$  (in radial direction). The average grain volume values are in the 1.2 E+3  $\mu\text{m}^3$  range. For hydrided alloy, the  $\alpha$ -Zr grain volumes (up to 5 E+3  $\mu\text{m}^3$ ) are slightly increased in comparison with as received alloy.

This thing is due to the heat treatment ( $T \approx 450^\circ\text{C}$ ) intended for hydrogen homogenization in material. The Zr-2.5%Nb recrystallization temperature threshold is around value  $T_{\text{th}} = 445^\circ\text{C}$ .

#### 4. CONCLUSIONS

The frequency dependence of attenuation coefficient in Zr-2.5%Nb alloy was measured in limit of experimental measurement errors, and the scattering coefficient was calculated. The hydrogen presence and grain size increase determine the attenuation increase. The experimental data were fitted to the



Rayleigh region scattering. The experimental results obtained with ultrasonic spectroscopy in grain size evaluation, have been compared with those obtained by metallographic analysis (ASTM E112). The good agreement between them indicates that this method can be used in non-destructive evaluation of grain size for nuclear materials. The reverse problem is: using the determined grain size we can evaluate the elastic coefficients.

## REFERENCES

1. P.Petculescu, R.Ciocan, *Investigation of the Austenitic Structures by Ultrasonic Spectral Analysis*, European Conference NDT'98 and in Journal of Nondestructive Testing and Ultrasonic, **3**, 11, (1998).
2. S. Hirsekorn, *The scattering of ultrasonic waves in polycrystalline materials with texture*, Journal of the Acoustical Society of America **77**, (1985).
3. E.P. Pappadakis, *Scattering in polycrystalline media*, Methods of Experimental Physics, **19**.
4. R.S. Sharpe, *Research techniques in nondestructive testing*, Academic Press, London, New York, 1970.
5. P. Petculescu, G. Prodan, R. Zagan, *An automated algorithm for simultaneously determining ultrasonic velocity and attenuation*, Rom. Journ. Phys., **50**, 7–8, 691–700 (2005).
6. J. Krautkrämer, H. Krautkrämer, *Ultrasonic Testing of Materials*, Spinger-Verlag, 1990.
7. P. Petculescu, C. Oprea, *Comparison of Two Ultrasonic Methods for Materials Characterisation*, Word Conference NDT, Roma, 2000.
8. Joseph L. Rose, *Ultrasonic waves in solid media*, Cambridge University Press, 2006.
9. Rohn Truell, *Ultrasonic methods in Solid State Physics*, Academic Press, New York.
10. Fedor I. Fedorov, *Theory of Elastic Waves in Crystals*, Plenum Press, New York, 1968.
11. Y.-M. Cheong, *Determination of anisotropic elastic moduli of Zr-2.5Nb CANDU pressure tube materials*, Journal of Materials Science, **35**, 1195–1200 (2000).
12. D.O. Northwood, *Elastic Constants of Zirconium Alloys*, J.of Nuc. Mat., **55**, 299–310 (1975).
13. Charles Kittel, *Fizica Corpului Solid*, Editura Tehnică, București, New York, London, 1969.
14. P.E. Danielson, *Zirconium and Hafnium and Their Alloys*, Metals Handbook, 9th Edition, Volume 9 (Metallography and Microstructures), American Society for Metals, pp. 497–502.