Hydride Concentration Assessment by Ultrasonics

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Abstract
Various ultrasonic (UT) methods, techniques, and transducers, used for CANDU reactor pressure tube inspection to detect areas with increased hydride concentration, estimate its level, and determine the hydride platelet features (dimensions, orientation, and spacing), are described and analyzed. Obtained results (theoretical and experimental) have demonstrated that using ultrasound, it is quite possible to perform a rapid screening to detect tube areas with increased hydride concentration and estimate hydride level. These results showed that using UT signals in the time and frequency domains, the hydrided areas with concentration about 15ppm can be distinguished.

Keywords: ultrasonic inspection, novel techniques and probes, improved hydride detection.

1. Introduction and Description of Hydride Platelets

During CANDU reactor operation the pressure tube (PT) material - zirconium alloy - absorbs hydrogen isotopes (hydrogen and deuterium) that can appear due to the radiolysis of water used as coolant agent or due to heavy water according to the reactions

$$\text{H}_2\text{O} \rightarrow \text{H}_2 + \text{O} \quad \text{and} \quad \text{D}_2\text{O} \rightarrow \text{D}_2 + \text{O}$$

(1)

Also, hydrogen and deuterium can appear due to oxidation of zirconium alloys

$$\text{Zr} + 2\text{H}_2\text{O} \rightarrow \text{ZrO}_2 + 2\text{H}_2 \quad \text{and} \quad \text{Zr} + 2\text{D}_2\text{O} \rightarrow \text{ZrO}_2 + 2\text{D}_2$$

(2)

Hydrogen and deuterium in solid solution diffuses due to the existence of concentration, temperature and stress gradients. A significant concern is the absorption of deuterium and hydrogen into the bulk of the PT during in-service operation. This has major economic and safety considerations: once absorbed, the deuterium and hydrogen are dissolved in solid solution and precipitate as deuterides or hydrides (henceforth called hydrides) in the form of platelets (which are typically “needles” or thin plates of a single orientation and habit), when saturation is reached or temperatures are lowered. Note that total hydride concentration is typically measured as a sum of the hydrogen weight concentration and half of the deuterium weight concentration (i.e. H+D/2, because deuterium is twice heavier).

Analyzing data from many sources [1-5], it was found that at shutdown conditions in reactor the hydride platelets are typically uniformly distributed and randomly oriented along the bulk of pressure tubes. The normal hydride concentration in tubes removed from a reactor lies within the range (5-40)ppm. Tube specimens artificially hydrided in laboratory contained H concentration from 20ppm to 300ppm. (Unit “ppm” is the hydrogen by weight in parts per million of tube material).

Typical hydride morphology, reproduced from [4-6], is shown in Figs. 1a-1b (optical microscope image and electronic microscope image. Average length of hydride platelet (two graphs based on the results from [1-5]), is shown in Fig 2.
Figure 1. a - optical microscope image showing the hydride morphology and distribution at magnification x 100 and hydride concentration ~20ppm, b - electronic microscope image showing the hydride morphology and distribution at hydride concentration ~80ppm.

Figure 2. Hydride platelets average length vs. total hydride concentration. Solid line - tubes removed from reactor, dashed line - artificially hydrided tube specimens.

Typically hydrides form in long platelets (slabs), mainly parallel to each other and oriented in some preferential direction: circumferential or radial. These platelets are about ~100-500µm long depending on the concentration (see Fig. 2), ~10-50µm wide, and ~1-2µm thick. Platelet slabs are usually more or less evenly (uniformly) distributed within the hydrided area with spacing about platelet length (see Figs. 1a-1b above).

The hydride platelets make tubes brittle, decrease their fracture toughness, and reduce strength of the material. This can cause operating problems such as delayed hydride cracking and hydride blistering, which can and have led to pressure tubes leaks and failures. The hydrogen isotope concentration in reactor PT, particularly in the rolled joint (RJ) regions, increases with operating
time because of uptake from water corrosion, pick up from heavy water coolant, and ingress from the annulus gas. When the garter springs separating the PT and calandria tube are misplaced, resulting in contact between the two tubes, then a cold spot forms on the PT and the hydride migrates to and precipitates at the cold spot which might lead to the formation of a blister.

These problems are currently a life-limiting factor in CANDU reactors. They have already led to premature re-tubing of reactors at a cost of several hundred million dollars. A non-destructive method of measuring the hydride concentration in PT is of great interest, since it would allow selective, rather than complete, re-tubing of the reactors, thus presenting a large cost saving.

2. **Non-Destructive Means of Measuring Hydrogen Content in PT**

Current methods of measuring hydrogen/deuterium in PT leave much to be desired [1-2]. Originally, tubes were removed and analyzed. In addition, various non-destructive techniques have been investigated for measuring hydride concentration: eddy-current testing, neutron radiography, nuclear acoustic resonance, internal friction, resistivity measurement for hydrogen terminal solid solubility (TSS) temperature determination, ultrasonic (UT) techniques, laser-UT method, and others.

2.1. **Eddy-current resistivity measurement**

Good results (in terms of accuracy and minimum hydrogen concentration detection) have been obtained using eddy current resistivity measurement over heating cycle for Terminal Solid Solubility (TSS) determination [7-9]. The technique allows measuring as low as ~10ppm bulk hydrogen equivalent concentration and higher with error about a few ppm. However, this system has serious limitations and disadvantages. First of all, it is very complex (seal assembly, bladder assembly, water compressor pump, water extraction pump, eddy current probe, contact thermocouple assembly, induction heating coil, pressure relieve valve, and probe deployment cylinder). Moreover, this method needs contact eddy current probe and contact thermocouple placed on the inner surface of the PT. In addition, this technique is very slow (~90 minutes for one location measurement) and has a high cost. Besides, the (TSS method cannot distinguish between H and D, it does not work in the RJ areas, and sometimes it requires a very high temperature (greater than 350°C, which might alter the PT material). Last but not the least, the results of TSS measurements depend on the PT material microstructure, which in turn depends on the PT age, total radiation dose, number of thermocycles, and other factors.

2.2. **Scrape sampling and their mass-spectroscopic analysis**

Scraping technology is probably the most accurate method of hydride concentration measurement. Scrape tool removes thin slices of the ID surface of PT for chemical analysis to measure hydrogen isotope content. However, useful as it is, this technique is not non-destructive, it can potentially lead to some structure integrity problem, requires significant radiation dose to perform, it is near-surface only, it is slow, and has a high cost. Moreover, the equipment and process of mass-spectroscopic measurements of hydride concentration in the scrapes are very complex and expensive, while at the same time, the uncertainty of measurements is not very good: it is about 5%.
2.3. Electromagnetic methods

Electromagnetic methods allow determining the electrical conductivity of ZrNb alloys with different quantities of absorbed hydrogen [10-15]. These techniques are widely used for hydride detection and provide rather good sensitivity. However, the tests to be accurate should be based on multiple statistical measurements due to the weak signals, low signal/noise ratio, and many perturbing factors: microstructure inhomogeneity, tube age, radiation field, temperature, and others. In addition, since tests can be performed only at low frequency, the response signal is very sensitive to any random changes in the material electrical conductivity and magnetic permeability. Besides, the effect of the probe lift-off leads to the substantial additional errors of measurements.

2.4. Ultrasonic testing

UT method is probably the most promising technique to rapidly screen a section of tube crossover, detect high hydride area, estimate concentration and hydride platelets features like length, thickness, orientation, and spacing. Recall that UT method is routinely used in-service for the PT inspection.

UT has several major advantages: it is sensitive, simple, convenient, safe, rapid, and inexpensive. UT is a volumetric method, frequently applied for material characterization, including texture, microstructure, morphology, whisker/fiber distribution, density variations, and grain size [16-17]. Various UT methods allow measuring different acoustic parameters of material: attenuation, coefficient, acoustic impedance, elastic moduli, acoustic velocities, density, characterization of inhomogeneities (hydride platelets, in our case) by back scattering, and others.

Assessment of hydrided areas in different materials by using UT waves are described in [18-24]. These techniques are based on the changes in the amplitude, time-of-flight and spectrum of the UT pulse, which occur due to scattering on the hydride platelets, when UT pulse passes through the hydrided area. Detection, characterization and sizing of hydrided areas and assessment of hydride platelets in Zircaloy and ZrNb are presented in [15, 21, 25-33] and references therein.

One of the UT methods for hydride concentration detection and measurement is the velocity ratio measurement [28-30]. This method uses the fact that the longitudinal velocity $C_L$ is higher and the shear velocity $C_S$ is lower in hydrided areas of PT compared to normal Zr-2.5%Nb material; hence the ratio $N$ of longitudinal to shear velocities $N=C_L/C_S$ increases as hydride concentration increases. Change in the velocity ratio $N$ is ~0.1-0.02%, when H concentration varies from ~10ppm (typical in normal material) to 40ppm. However, there are significant limitations to the detection capabilities of this method due to background intrinsic variations in the velocity ratio $N$ caused by other effects (e.g. initial and accumulated inhomogeneities and imperfections). Note also, that in any real experimental setup, the measured velocity ratio N will change depending on such factors as probe water path, tube wall thickness, probe angle orientation, and others, because these factors significantly affect beam trajectory and time-of-flight of the longitudinal and shear waves. As result, the paths travelled by these waves are different. Estimate shows that changes of the velocity ratio $N$ due to these factors are ~1-2%, i.e. they are ~10-100 times stronger than changes of the velocity ratio $N$ because of the hydrides presence. Also note that for isotropic materials $N=C_L/C_S=\sqrt{[2(1-\nu)/(1-2\nu)]}$, i.e. velocity ratio $N=C_L/C_S$ depends only on Poisson ratio $\nu$. Therefore, since the Poisson ratio $\nu$ varies insignificantly with hydride
concentration (because even at a high hydride concentration 100ppm, the hydride content is only about 0.01%, see section 3.1 below), then change in the velocity ratio \( N \) is also very weak.

A non-contact laser-UT methods have also been used for the hydride area assessment in Zircaloy tubes [10, 34-36]. A few papers were dedicated to analysis of the resonance scattering of UT waves on defects and inclusions [37-38].

There were also some investigations focused on the nonlinear effects. These effects are usually small, and so they have been a neglected weapon in the arsenal of UT methods. However, in some cases nonlinear properties are fairly sensitive to variations in material microstructure [5, 39]. Investigation of nonlinear phonon-phonon resonance interaction shows that this technique could be potentially useful and hydride areas with concentration greater than 100ppm might be detectable. However, in general the results of hydride detection with the help of nonlinear acoustic effects are inconclusive.

Generically, the results, presented in [15, 21, 25-33] and references therein, clearly demonstrate that different UT techniques, wave modes, transducers, and parameters of the received UT pulses can be used for hydride assessment and characterization. But the most sensitive and efficient techniques are based on the usage of shear backscattered, reflected, and transmitted waves.

### 3. Theoretical Background

#### 3.1. Characteristics of hydride platelets

It is very important from theoretical and practical points of view to understand and estimate the various factors that can affect backscattered UT signals from hydrided areas of PT.

Table 1, based on results presented in [1-6], shows that that differences of the mechanical elastic characteristics of the PT material ZrNb and hydrides are not small. Since the acoustic parameters of the material are determined by its elastic characteristics, the differences between the acoustic properties of the PT material and hydrides are also significant, see Table 2.

<table>
<thead>
<tr>
<th>Material Characteristic</th>
<th>Material</th>
<th>PT alloy Zr-2.5%Nb</th>
<th>Hydride Zr-1.7%H</th>
<th>Difference in relation to PT, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s modulus ( E ), GPa</td>
<td>91</td>
<td>59</td>
<td>~35</td>
<td></td>
</tr>
<tr>
<td>Poisson ratio ( \nu )</td>
<td>0.333</td>
<td>0.426</td>
<td>~28</td>
<td></td>
</tr>
<tr>
<td>Shear modulus ( G ), GPa</td>
<td>34</td>
<td>20</td>
<td>~41</td>
<td></td>
</tr>
<tr>
<td>Bulk modulus ( K_b ), GPa</td>
<td>97</td>
<td>134</td>
<td>~38</td>
<td></td>
</tr>
<tr>
<td>Lame constant ( \lambda ), Gpa</td>
<td>74</td>
<td>120</td>
<td>~62</td>
<td></td>
</tr>
<tr>
<td>Lame constant ( \mu ), Gpa</td>
<td>34</td>
<td>20</td>
<td>~41</td>
<td></td>
</tr>
</tbody>
</table>
Table 2. Acoustical properties of pressure tube material ZrNb and hydrides

<table>
<thead>
<tr>
<th>Material</th>
<th>PT alloy Zr-2.5% Nb</th>
<th>Hydride Zr-1.7%H</th>
<th>Difference in relation to PT, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Longitudinal radial velocity $C_L$, mm/µs</td>
<td>4.71</td>
<td>5.39</td>
<td>~14</td>
</tr>
<tr>
<td>Shear radial velocity $C_S$ polarized circumferentially, mm/µs</td>
<td>2.35</td>
<td>1.93</td>
<td>~18</td>
</tr>
<tr>
<td>Density $\rho$, g/cm³</td>
<td>6.48</td>
<td>5.60</td>
<td>~14</td>
</tr>
<tr>
<td>Longitudinal impedance $Z_L = \rho C_L$, MRayl</td>
<td>31</td>
<td>30</td>
<td>~3</td>
</tr>
<tr>
<td>Shear impedance $Z_S = \rho C_S$, MRayl</td>
<td>15</td>
<td>11</td>
<td>~27</td>
</tr>
</tbody>
</table>

These differences in acoustic parameters should lead to the variations of the following parameters: refraction angles, reflection coefficients, beam trajectories, UT pulse times-of-flight, scattering, attenuation, signal amplitudes and spectra of the received signals. However recall, that even at a high hydride concentration 100ppm (see e.g. Fig. 2), the hydride content is only 0.01% of the total weight of PT material. Therefore, acoustic parameters of such material are almost equal to acoustic parameters of pure Zr-2.5%Nb.

The PT material Zr-2.5%Nb is not an isotropic one, it belongs to the so called cylindrical orthotropic materials, where the material properties in three mutually perpendicular directions (axial, radial, and circumferential) are different. Therefore, the respective elastic moduli are also different along three mutually perpendicular directions. Typically, an orthotropic material is characterized by three Young's moduli, three Poisson's ratios, and three shear moduli (see details in Attachment). It means, that strictly speaking, nominal PT material and hydrided areas have many different elastic and acoustic parameters, moreover characteristics of hydrided areas depend on the platelet concentration, orientation, shape, spacing and dimensions. In other words, various hydrided areas will have different elastic and acoustic parameters.

In the PT material there are in total nine different types of UT waves with various parameters including speeds of propagation (velocities). There are three different modes of acoustic waves in each of three different directions:

1. Waves propagating in the radial direction (1): longitudinal wave $C^{(1)}_L$, shear wave polarized circumferentially $C^{(1)}_{S2}$, and shear wave polarized axially $C^{(1)}_{S3}$.
2. Waves propagating in the circumferential direction (2): longitudinal wave $C^{(2)}_L$, shear wave polarized axially $C^{(2)}_{S3}$, and shear wave polarized radially $C^{(2)}_{S1}$.
3. Waves propagating in the axial direction (3): longitudinal wave $C^{(3)}_L$, shear wave polarized circumferentially $C^{(3)}_{S2}$, and shear wave polarized radially $C^{(3)}_{S1}$.

The measured values of different velocities (speeds of propagation) of longitudinal and shear UT waves propagating in various directions in Zr-2.5%Nb are presented below in Table 3 in mm/µs.
Table 3. Longitudinal and shear velocities of various UT wave modes (in mm/µs) in Zr-2.5%Nb.

<table>
<thead>
<tr>
<th>Direction of polarization</th>
<th>Direction of propagation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radial</td>
<td>Longitudinal C_s^(1L)=4.715</td>
</tr>
<tr>
<td>Axial</td>
<td>Shear C_S^s(1)=2.29</td>
</tr>
<tr>
<td>Circumferential</td>
<td>Shear C_S^s(2)=2.39</td>
</tr>
</tbody>
</table>

Thus, we can use various UT methods and techniques, nine different modes of the UT pulses and measure various parameters of each pulse: amplitude (characterizing the attenuation of UT pulse during its propagation and reflection/scattering from hydride platelets), time-of-flight (characterizing the trajectory and speed of propagation of the UT pulse), and spectrum (characterizing the attenuation of UT pulse during its propagation as a function of frequency.

As Table 2 shows, the response amplitude may be greater or smaller for the hydrided area in comparison with the area of low hydride content, depending on the probe position and orientation. For example, because of a small shear acoustic impedance of the hydrided area, the pressure transmission coefficient at the interface water/tube is about ~30% greater for the hydrided area. As result, the amplitude of the shear wave response can be stronger for the hydrided area than for the clean area of the tube. But on the other hand, the hydride platelets scatter and slightly attenuate the UT waves, transmitted through the PT wall, therefore the amplitude of the shear wave response can be weaker for the hydrided area. The final result depends on the balance of these two conflicting effects.

3.2. Scattering by a single hydride platelet

Using data presented in Table 2, it is easy to calculate the pressure reflection coefficient \( R_s \) for shear UT wave at the interface ZrNb/hydride:

\[
R_s = \frac{(Z_s^{ZrNb} - Z_s^{hydride})/(Z_s^{ZrNb} + Z_s^{hydride})}{(15-11)/(15+11)} \approx 0.15 ,
\]

where \( Z_s^{ZrNb} \) and \( Z_s^{hydride} \) are the respective shear wave acoustic impedances.

For longitudinal waves the pressure reflection coefficient \( R_L \approx 0.016 \), i.e. \( R_L \) is ten times smaller than \( R_s \); it means we should use only shear waves for hydride platelets detection in ZrNb tubes. However, taking into account a wave mode conversion at the interface ZrNb/hydride, we can also use the longitudinal waves.

Using typical dimensions of hydride platelets (see Fig. 2), we can calculate scattering on them using formulae for Mie scattering, because in our case we are in the region where \( k r \approx 1 \), where \( k = 2\pi/\lambda \) is the wave number of UT pulse, \( \lambda \) is the UT wavelength, and \( r \) is the average “radius” of spherical hydride platelet. Recall that actual platelets are slabs with three different dimensions, therefore scattering on such obstacles is more complex than scattering on the spherical obstacles.

In our case, we are analyzing scattering on typical platelets (slabs) with length \( r \approx 0.03-0.09\)mm at typical concentrations 20÷60ppm (see Fig. 2) and typical wave number \( k \approx 30÷60\)mm\(^{-1}\) for shear wave in ZrNb at UT frequency \( f = 10÷20\)MHz.
Scattering in the Mie region is the most difficult to calculate. However, we will approximately use for our calculations the well-known formulae for Rayleigh scattering region, where strictly speaking \( kr << 1 \). In other words, we assume that in our case the UT wavelength \( \lambda \) is greater than platelet size \( r \), and that scattering is weak, so that the scattered pressure is much less than the incident pressure. This assumption of weak scattering (known as the Born approximation), implies that multiple scattering can be ignored.

If we could consider that scatterers (i.e. our hydride platelets) are rigid, then it would not be difficult to calculate the reflected pressure by using formula (1), knowing hydride concentration, assuming some average shapes, dimensions, orientation, and spacing of platelets, and considering that there is no mode conversion.

However, in reality the hydride platelets are compressible, i.e. they are the elastic scatterers. Therefore, the scattered pressure \( P_{\text{scat}}(r, \theta) \) from a single hydride platelet and its effective differential (i.e. depending on angle) scattering cross-section \( \sigma(\theta) \) (ratio of scattered power in watts to intensity of the incident wave in watts per \( m^2 \)) are respectively equal to [39-42]:

\[
P_{\text{scat}}(r_0, \theta) = P_{\text{inc}} \exp(-jk r_0) \frac{k^2 V}{4\pi r_0 \kappa} \left( \frac{k^2 - \kappa^2}{\kappa^2} \right) + \frac{\rho - \rho_0}{\rho} \cos \theta,
\]

(2)

\[
\sigma(\theta) = \frac{V^2 \pi^2}{\lambda^4} \left( \frac{k^2 - \kappa^2}{\kappa^2} \right) + \frac{\rho - \rho_0}{\rho} \cos \theta
\]

(3)

where \( P_{\text{inc}} \) is pressure in the incident UT wave, \( k = \frac{2\pi}{\lambda} \) is the wave number of UT pulse, \( \lambda \) is the UT wavelength, \( V \) is the platelet volume, \( r_0 \) is the distance between platelet and UT probe, \( \theta \) is the angle between incident and scattered waves, \( \rho \) is the ZrNb density, \( \rho_0 \) is the platelet density, \( K = 1/\rho C^2 = 1/K_0 \) is the ZrNb compressibility, \( K_0 = 1/\rho_0 C_0^2 = 1/K_{00} \) is the platelet compressibility, \( K_b \) is the bulk modulus of ZrNb, \( C \) is the speed of propagation of UT shear wave in ZrNb, \( K_{00} \) is the bulk modulus of platelet, \( C_0 \) is the speed of propagation of UT shear wave in platelet.

Formula (2) shows that term \( \exp(-jk r_0)/4\pi r_0 \) describes spherical diverging wave during its propagation from probe to hydride platelet and back. This wave has decreasing amplitude. For an infinitely dense and rigid (incompressible) platelet formula (2) will be significantly simplified.

Formulae (2) and (3) show that terms \( k^2 V = V(2\pi/\lambda)^2 \) and \( V^2/\lambda^4 \) are decreasing when \( \lambda \) increases, i.e. UT wave does not “notice” platelets with small dimensions.

Formulae (2) and (3) show that terms \( (K-K_0)/K \) and \( (\rho-\rho_0)/\rho \) describe a scattering area, where compressibility and density change, and therefore this area reflects the incident UT wave. The compressibility term \( (K-K_0)/K \) is independent of angle \( \theta \), and is referred to as a monopole term since it corresponds to a pulsating point source (i.e. platelet pulsates: expands and contracts).

On the other hand, the density term \( (\rho-\rho_0)/\rho \) is angle-dependent and is known as the dipole term because it arises from oscillatory motion like a dipole source (i.e. platelet oscillates back and forth about the undisturbed position). Thus, one can see that mismatches in the mechanical properties will cause the obstacle to undergo different modes of vibrations. Note that for hydride platelets, the compressibility term is more significant.
3.3. Scattering by an ensemble of platelets

The complex structure of hydrided areas of PT can be described by using two different models. The first model is based on the assumption that acoustic properties of the hydrided area vary in continuous manner and that scattering is caused by the changes in elastic and acoustic parameters of this area encountered by the incident wave. The other model is based on the assumption that hydrided area consists of a distribution of discrete scatterers imbedded in a background (nominal PT material) whose acoustic properties are constant.

The first model is rather easy to analyze, if acoustic parameters of hydrided area are known. In such continuum model the variations in the acoustic properties in the hydrided area are assumed to create the respective reflection of the incident wave. Usually, a standard UT probe cannot resolve signals scattered by neighboring platelets that are separated by distance less than $\lambda/5$, therefore the hydrided area is actually looks highly homogeneous to a UT transducer. Thus, the hydrided area behaves as though it has a uniform density and compressibility which differ from that of the medium outside this area (i.e. nominal PT material). This difference will produce scattering (or reflection and refraction) of the incident UT wave.

However recall, that actual difference in average acoustic properties of the hydrided and non-hydrided areas is very small, because the hydride concentration is also very small (only about 0.01%), as it has already been mentioned earlier in section 3.1. Moreover, the hydrided area has many different elastic and acoustic parameters due to anisotropy, and in addition, the acoustic characteristics of hydrided area depend also on the platelet concentration, orientation, shape, spacing, and dimensions. It means that it is not easy to estimate what values of elastic and acoustic parameters should be used to describe properties of various hydrided areas.

In the second model (particle approach), the scatterers (hydride platelets) are assumed to be discrete entities perhaps with varying geometry and differing acoustic properties, and to have a certain spatial distribution. As result, the UT signals, reflected from different platelets, have scattering contributions which can constructively and/or destructively interfere. In this model to calculate the scattered pressure wave, one should make the following approximations: platelets are considered identical in their dimensions, shape, spacing, orientation, and acoustic properties; scattering is weak, and multiple scattering can be ignored; platelet concentration is on average space invariant within the insonified volume; and platelets are randomly distributed.

If scatterers are randomly distributed, then the position of each platelet would be uncorrelated with any other, and the scattered power should increase with the platelet concentration leading to the incoherent scattering. On the other hand, correlation between the platelet positions (implying strictly fixed spatial and temporal positions of platelets) results in interference effects leading to the coherent scattering. Significant additional complications will appear if we take into account that in a real situation the platelets have different size, shape, spacing, acoustic properties, packing factor, concentration and orientation.

Thus, the positions of any pair of platelets are partially correlated, i.e. they are neither uncorrelated, not perfectly correlated. It leads to the partial coherence of the received signals, and this case is the most difficult one for calculations. Therefore, we should take into account both components of the partially coherent backscattered UT signal: coherent and incoherent.
For incoherent scattering the correlation function between reflections from platelets is negligibly small. Therefore, acoustic intensities of signal backscattered from different platelets are additive, i.e. the whole intensity $I_{\text{incoherent}}$ of the incoherent backscattering signals is equal to

$$I_{\text{incoherent}} = \sum_n |P_n|^2, \quad P_n = A_n \exp[i(k_n r_n + \omega_n t)]$$

where $P_n$ is the pressure of wave reflected from $n^{th}$ platelet, $A_n$ is the amplitude of this wave, $k_n$ is the wave number, $\omega_n$ is the angular frequency, $r_n$ is the distance between $n^{th}$ platelet and UT probe, $t$ is the time.

For coherent scattering, the pressures of reflected waves are additive, i.e. the whole intensity $I_{\text{coherent}}$ of the coherent backscattering signals is equal to

$$I_{\text{coherent}} = \sum_n |P_n|^2$$

As result, the total intensity of scattered UT signal is the sum of two terms (4) and (5).

### 3.4. Resonance scattering by platelets

Typically the scattering intensity from hydride platelets is rather weak. However, it can be significantly increased in case of the resonance excitation of characteristic oscillations and vibrations of the elastic (compressible) platelets. If hydride platelet undergoes the forced oscillations and vibrations in the field of the primary incident wave, then scatterer can radiate as monopole or dipole or quadrupole when driven at a resonant frequency, because the scattering body is caused to vibrate as in its corresponding natural mode of free vibration.

The resonant frequency $f_{\text{res}}$ of hydride platelet, damped by surrounding medium (ZrNb) can be estimated [44] by using formula

$$f_{\text{res}} = \frac{V_{\text{platelet}}}{2\pi D} \sqrt{\frac{3\rho_{\text{platelet}}}{\rho_{\text{ZrNb}}}},$$

where $V_{\text{platelet}}$ is the velocity of UT wave (shear or longitudinal) in hydride platelet, $D$ is the diameter of spherical hydride platelet (if platelet is a slab, then a respective typical size, e.g. length, should be used instead of $D$), $\rho_{\text{platelet}}$ is the density of platelet, and $\rho_{\text{ZrNb}}$ is the density of PT material.

Using formula (6), and data from Table 2, the respective values of resonance frequency $f_{\text{res}}$ for shear wave and typical hydride platelet lengths, corresponding to typical hydride concentrations, were calculated and presented in Table 4. Data shown in Table 4 are based on the Fig. 2 and approximations and assumptions presented in [1]: uniform platelets distribution, their shape, orientation, spacing, and typical cooling rate ~1.5 deg/min during reactor shutdown. Note that resonance frequency $f_{\text{res}}$ of hydride platelet can be also estimated by using very simple but approximate formula based on the idea that at the resonance frequency the average length $L$ of “free” platelet should be equal to half-wavelength, i.e. $L = \lambda/2$. In this case, the respective $f_{\text{res}}$ for “free” platelet will be equal to

$$f_{\text{res}} = \frac{V_{\text{platelet}}}{2L}$$
The results of calculations of values $f_{\text{res}}$ based on formula (7) are also presented in Table 4. These values are approximately twice greater than $f_{\text{res}}$ values calculated using formula (6). Most probably, the reason is that real hydride platelets in PT are strongly damped by surrounding main material (ZrNb), and therefore formula (6) is more accurate than formula (7), and the respective real resonance frequency is lower.

Table 4. Hydride concentration, respective average platelet length, and respective average resonant frequencies of shear waves.

<table>
<thead>
<tr>
<th>Hydride concentration, ppm</th>
<th>Respective platelet length, μm</th>
<th>Respective resonance frequency of shear UT wave based on formula (6), MHz</th>
<th>Respective resonance frequency of shear UT wave based on formula (7), MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>110</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>80</td>
<td>105</td>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>60</td>
<td>100</td>
<td>6</td>
<td>11</td>
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4. Experimental Results

4.1. Angle shear wave probes working in pitch-catch mode
The most sensitive and reliable results can be obtained using pitch-catch (PC) angle shear wave method and changes in parameters of the UT wave scattered on the hydride platelets (see Figs. 1-2), particularly when the resonant scattering occurs, i.e. when the average length of the platelet (which usually is about ~20-80μm depending on concentration), equals to the half-wavelength of the UT wave (recall that in the PT material the half-wavelength of 20MHz shear wave is about ~50μm).

In the “as received” PT, the hydride concentration is ~5-15ppm, while in tubes in reactor this concentration lies within the range ~15-100ppm (where unit “ppm” is hydrogen by weight in parts per million parts weight of tube material).

![Figure 1. Schematic of shear wave angle PC technique with a large incident angle showing a long trajectory of the UT beam propagating within the PT wall.](image-url)
Figure 2. Schematic of angle PC method using transmitted shear UT waves, where the hydride platelets (a) scatter and slightly attenuate the UT waves, transmitted through the PT wall. Compare with PT area without hydride platelets (b), where all UT waves are transmitted through the PT wall.

Experimental investigation was performed using calibrated, computerized scanning UT system containing water tank, Winspect data acquisition software, SONIX STR-8100 digitizer card, and UTEX UT-340 pulser-receiver. UT probes with different frequencies, focal lengths, and diameters, positioned circumferentially in the PC mode at various water-paths and incident angles, were used for testing. 2D B-scans were performed in the axial direction.

Experiments showed that for hydried areas with concentration about 40ppm and 80ppm in comparison with non-hydried areas, the total signal amplitude varies about ~10%, see Figs. 3-5. Note that axial and circumferential dimensions of the insonified examination area are about 10x10x10mm$^3$.

Figure 3a. PC shear wave axial B-scan of the PT sample with 80ppm hydride concentration band (see arrows) located from -40mm to +5mm. Probes: center frequency f=20MHz, aperture diameter D=9.5mm, focal length F=33mm, water-path WP=25mm, incident angle $\alpha=32^\circ$. 
Figure 3b. PC shear wave axial B-scan of PT sample with 40ppm hydride band (see arrow) located from -40mm to -10mm. Probes: f=20MHz, D=9.5mm, F=25mm, WP=33mm, $\alpha=32^\circ$.

Figure 4a. PC shear wave axial B-scan of the PT sample with 60ppm hydride band (see arrows) located from -20mm to 0mm. Probes: f=20MHz, D=9.5mm, F=33mm, WP=25mm, $\alpha=32^\circ$. 
Figure 4b. PC shear wave axial B-scan of PT sample with 100ppm hydride concentration band located from -50mm to -5mm. Probes: f=20MHz, D=9.5mm, F=33mm, WP=25mm, $\alpha=32^\circ$.

Figure 5. Pitch-catch shear wave axial B-scan (signal is rectified) of PT sample with three hydried bands: 20ppm hydride concentration band located at z<0mm, 60ppm band at 0<z<50mm, 40ppm hydride concentration band at 50<z<100mm, and non-hydried band at z>100mm. Probes: f=20MHz, D=9.5mm, F=33mm, WP=25mm, $\alpha=32^\circ$. 
It is obvious that response changes, related to the hydride concentration, are weak (see Figs. 3-5). At the same time, signal fluctuations due to background intrinsic material variations (e.g. initial and accumulated inhomogeneities such as oxide and flaws) and various changes in surface roughness and material microstructure (e.g. grain size, material morphology, imperfections, etc.) might be significant. This type of noise is inherent to the PT, and can never be completely suppressed. So the challenge is to distinguish a weak signal variation, related to hydride concentration, on the background of fluctuations due to the structure noise.

More sensitive and reliable results can be obtained using changes, caused by the hydride platelets scattering in the signal spectrum, particularly when the resonant scattering occurs. In general, the UT spectroscopy is widely used for qualitative and quantitative microstructure characterization. Analysis of the UT spectral features can yield quantitative correlations with material properties that are governed in turn by material microstructure. The UT pulse, passed through the insonified area of the test object, contains information related to the area physical characteristics, inhomogeneities, and other features. Therefore, the obtained “spectral signature” of the received UT pulse, passed through test object, depends on the material parameters of this object, shape, size, composition, integrity, elastic properties, internal imperfections (e.g. hydride platelets), and other factors.

Anything that affects the material characteristics, also affects spectrum of the obtained UT response. Such spectrum represents intrinsic characteristics of the insonified area of the test object; it is the “fingerprint” of this object. Appropriate usage of information contained within the spectrum and identification of its features can serve as a powerful tool for test object characterization.

The resonant scattering occurs when the UT frequency equals to the resonant frequency of hydride platelets (i.e. when platelet length equals to the half-wavelength of the UT signal), then the maximum scattering on the platelets occurs. It will lead to the maximum difference between the amplitude and spectrum of the acoustic pulses passed through the hydrided and non-hydrided areas.

When the UT waves with resonant frequencies of the platelets are scattered on these platelets, then contribution of these frequencies in the spectrum of the received UT pulse (passed through PT wall thickness and reflected from the PT OD) is weaker for the hydrided area. Respectively, the obtained spectrum is shifted to the low-frequency area, see Figs. 6 and 7.

Fig. 7 below shows how maximum frequencies in the response spectra on Fig. 6 depend on the hydride concentration.

Note that results presented above in Figs. 6-7, were obtained extracting the A-scans for the non-hydrided bands and hydrided bands. Then, using Winspect software, their spectra were derived.

Typically, we can expect a range of hydride platelet sizes, spacing, and orientation (radial and circumferential), which will complicate the process of the measurements and analysis.
Figure 6. Spectra of four rectified A-scans derived from PC shear wave axial B-scan of PT with three hydrided bands: non-hydrided band, 20ppm hydride concentration, 40ppm concentration, and 60ppm concentration. Probes: $f=20$MHz, $D=8$mm, flat, WP=20mm. For hydrided bands the high-frequency contribution within the range 11-32MHz is significantly smaller than for the non-hydrided area.
It is estimated, that hydride areas with concentration difference ~10ppm can be distinguished ultrasonically. At the same time, the UT methods, due to some principal limitations (pretty large wavelength in comparison e.g. with X-ray method), can be employed only as screening techniques to scan the whole PT in search of the areas of high hydride accumulation and were intended to be used in advance of the accurate point measurement such as scrape sampling or TSS measurement.

4.2. Normal beam probes working in pulse-echo mode
Second series of experiments was performed by using almost normal beam (NB) probe, oriented at small incident angle, with multiple shear OD reflections. Schematic and Imagine-3D simulations of these experiments presenting backscattered, reflected, and transmitted waves are shown in Figs. 8-11. Note that dimensions of the examination area are about 5x5x5mm³.

Note that reflections from hydride platelets are usually very weak. Respectively, due to these reflections, the attenuation effect for UT wave passing through hydried area is also weak, but it is much stronger for the UT wave which undergoes multiple OD/ID reflections. When UT beam passes many times through the hydried area (i.e. when the beam trajectory in the hydried area is lone enough), then even the extremely weak changes lead (due to the “feature accumulation” effect after multiple reflections of UT wave within the tube wall) to some also weak but already distinguishable features of the received UT response.

This effect can be called the “self-amplification” of a weak feature: it is similar to the constructive interference. During material characterization (and hydride detection is a typical process of the material characterization), this “feature accumulation” effect achieves maximum efficiency approximately at the 10th reflection, because the UT beam, passing through the area of material with specific physical parameters, “feels” their influence many times.
Figure 8. Schematic of almost NB technique with multiple OD reflections.

Figure 9. Schematic of method using backscattered UT waves, where the hydride platelets reflect the UT waves back to the transducer. This reflection is usually weak, see just a few purple reflected rays returning to the transducer.

Figure 10. Schematic of method using the OD reflected UT waves, where the hydride platelets on the left image scatter and slightly attenuate the reflected UT waves returning back to the probe. Compare with PT area without hydride platelets (on the right image), where all UT waves reflected from the PT OD are returning back to the transducer. This attenuation effect is weak, but it is much stronger for the UT wave with multiple OD/ID reflections, see Fig. 11.
Experiments showed that for the hydrided areas with concentration about 40ppm and 80ppm in comparison with non-hydrided areas, the total signal amplitude of shear wave after multiple reflections is about ~10-15% greater. Recall, that most probably it happens because of a small shear acoustic impedance of the hydrided area, which leads to a greater amplitude of the shear wave response.

However, more sensitive and reliable results can be obtained using changes, caused by the hydride platelets scattering in signal spectrum, particularly when resonant scattering occurs. Using the obtained B-scans, a few A-scans were extracted for the non-hydrided and hydrided areas for signals related to the 12th shear wave OD reflection. Then, using Winspect software, their spectra were obtained; typical spectra for the non-hydrided and hydrided areas are shown in Figs. 12-14. It turned out that contribution of the high frequencies is definitely smaller for the hydrided areas. It confirms the assumption that due to the resonant scattering on the hydride platelets, the spectrum of the 12th shear wave OD reflection should be shifted to the low-frequency area. Emphasize that Fig. 13 shows the relative sizes of the high frequency areas (the dashed areas within the range 22-32MHz) of the response spectra for the PT coupons with different hydride concentration presented in Figs. 12 and 13. At the same time note that shear wave OD reflection is a rather weak signal; particularly it will be a challenge for the high frequency UT wave and long cable lengths of PT inspection systems. Therefore, this technique may have some difficulties in the field conditions.

Note that the hydride platelets are usually distributed inside the whole range of the platelet characteristics: shapes, length, thickness, orientation (circumferential or radial), concentration and spacing. However, it is known, that parameters of the received UT pulse (amplitude, spectrum, time-of-flight, refraction angle, trajectory, and others) should strongly depend on the platelet features. Moreover, it is reasonable to assume that using different UT methods and techniques (PC or PE, shear wave or longitudinal, circumferentially, radially or axially propagating waves, NB or angle beam, and others) and UT probes with different parameters (frequency, diameter, focal length, bandwidth, water-path, incident angle, and others), it is...
possible to correlate some parameters of the received UT responses with the hydride platelet features. As result, it will be possible to estimate different characteristics of the hydride platelets. In general, the employed UT technique and probes can and should be optimized for detection and assessment of the required type of hydrides.

Recall that in order to optimize the inspection process we should also determine the optimum parameters of the pulser-receiver (generator settings, such as shape, duration and amplitude of the excitation pulse; and receiver settings, such as amplification, bandwidth, etc.) and the required signal processing methods, such as filtering, averaging, cross-correlation, and others.

Figure 12. Spectra of two A-scans derived from NB axial B-scan of PT with 40ppm hydride concentration band. Probe: NB, f=20MHz, D=8mm, flat, WP=20mm. For hydrided area the high-frequency contribution of the shear wave OD reflection within the range 22-32MHz (dashed area) is approximately 2 times smaller than dashed area for the non-hydrided area.
Figure 13. Spectra of two A-scans derived from NB axial B-scan of PT with 80ppm hydride concentration band. Probe: NB, f=20MHz, D=8mm, flat, WP=20mm. For hydrided area the high-frequency contribution of the shear wave OD reflection within the range 22-32MHz (dashed area) is approximately 3 times smaller than dashed area for the non-hydrided area.

Figure 14. Relative size of the high frequency area (within the range 22-32MHz) of the response spectrum vs. hydride concentration.
Results of preliminary experiments, presented in Figs. 3-7 and Figs. 12-14, clearly demonstrate that using ultrasound, it is quite possibly to perform a rapid PT screening to detect areas with increased hydride concentration, estimate its level, and characterize hydride platelets.

It is obvious, that parameters of the received UT signals depend on the elastic moduli of the PT material, its microstructure and mechanical properties in the examined PT region. And of course, the opposite relationship is also true. For example, using known value of density $\rho$ for ZrNb and measuring nine different propagation speeds of UT waves (recall that ZrNb is an anisotropic orthotropic material), we can calculate all elastic moduli $E_{ij}$, $\nu_{ij}$ and $G_{ij}$ of ZrNb (see details in Attachment). Thus, performing analysis of different parameters of various UT waves, we can find correlations between elastic moduli and parameters of the received UT signals.

It is obvious, that presence of the hydride platelets and their features (concentration, dimensions, orientation and spacing) affect the elastic moduli of the PT material, its microstructure and mechanical properties. As result, performing analysis of different parameters of various UT waves, we can estimate the elastic moduli, microstructure and mechanical properties of PT material in the examined region. At the same time, different elastic, structural and mechanical properties should be related to the different characteristics of the hydride platelets. After that, we can find the optimum correlation (i.e. the strongest one) between the specified characteristic of the hydride platelet (length, thickness, orientation, spacing and concentration), which should be determined, and the measured optimal parameter of the optimum UT indication.

Finally, we can conclude that there is a large variety of different UT methods, techniques, wave modes, transducers, and parameters of the received UT pulses, which can be used for the hydride platelets characterization. The main challenge is to determine the optimal measured parameter of the optimal UT response, obtained using the optimal UT method, technique, wave mode, and transducer, which provide the most strong, reliable, and accurate correlation between the measured optimal parameter of the optimal response and the required hydride platelet feature, i.e. allows estimating this feature with maximum resolution, sensitivity and measurement accuracy.

5. **Conclusions**

1. Description and analysis of hydride platelets in PT is presented.
2. Different NDE techniques and means of measuring hydrogen content in PT are analyzed.
3. Various UT methods, techniques, and transducers, used for PT inspection with goal to detect areas with increased hydride concentration, estimate its level, and determine the hydride platelet features (length, thickness, orientation, and spacing), are described and analyzed.
4. Characteristics of hydride platelets, scattering by a single hydride platelet, scattering by an ensemble of platelets, and resonance scattering by platelets are analyzed.
5. Values of resonance frequency for typical hydride platelet lengths, corresponding to typical hydride concentrations, were determined.
6. Performed calculations show that using ultrasound, it is quite possible to detect tube areas with increased hydride concentration and estimate hydride level.
7. Two different techniques - angle shear wave probes working in the PC mode and NB probes working in the PE mode - were used for investigation.
8. Experiments on tube specimens, containing hydride with concentration step changes of 20, 40, 80 and 100ppm, confirm that all these steps can be detected, distinguished, and concentration level can be estimated.

9. Obtained experimental results demonstrate that UT signals in the time and frequency domains are very useful for hydride assessment.

10. Experiments show that hydrided areas with concentration ~15ppm can be distinguished.

11. Investigation shows that obtained UT responses are steady and robust to variations of tube wall thickness, surface condition, and probe position and orientation.

12. It is shown that main source of noise is the structure noise caused by variations in material microstructure (grain size, material morphology, two-phase \( \alpha - \beta \) structure of Zr-2.5%Nb alloy, imperfections, inhomogeneities, and so on). So the challenge is to distinguish the small signal variations, related to the hydride concentration, on the background of structure noise.

13. It is emphasized that is a large variety of different UT methods, techniques, wave modes, transducers, and parameters of the received UT pulses, can be used for the hydride platelets characterization.

14. There is a mutual dependance between parameters of the received UT signals and elastic moduli of PT material. For example, using known value of density \( \rho \) for ZrNb and measuring nine different propagation speeds of UT waves (recall that ZrNb is an anisotropic orthotropic material), we can calculate all elastic moduli of the material. In other words, performing analysis of different parameters of various UT waves, we can find correlations between elastic moduli of material and parameters of the received UT signals.

15. For further development it is necessary to increase accuracy and sensitivity of hydride level measurements, and improve signal/noise ratio.

6. References


33. A. Karpelson, “Hydride concentration screening in pressure tubes by ultrasonic

Attachment

Elastic Properties of Cylindrical Orthotropic Materials

For an orthotropic material (see e.g. [1]) the following elastic moduli are required: three Young's E₁, E₂ and E₃=E₅ and six Poisson's ratios ν₁₂, ν₂₁, ν₁₃, ν₂₃, and ν₁₅. In order to keep the elasticity tensor symmetric, the Poisson's ratios have to satisfy the relations νᵢⱼ/Eᵢ=νⱼᵢ/Eⱼ for all i≠j (no summation on dumb indices): Therefore, only 3 of the 6 Poisson's ratios are independent, because ν₂₁=(ν₁₂E₂)/E₁, ν₂₃=(ν₁₃E₃)/E₁, and ν₂₅=(ν₂₅E₅)/E₂.

The Young's modulus Eᵢ is a measure of the stiffness of the material, i.e. the resistance of the material to be deformed when a stress (uniaxial stretching or compression) is applied. The value is positive (Eᵢ > 0), and a larger value of Eᵢ indicates a stiffer material. The Poisson's ratio νᵢⱼ gives information about the ratio between lateral and longitudinal strain in uniaxial tensile stress. The Poisson's ratio measures the lateral contraction produced by the applied stress. When νᵢⱼ=1/2 the material is incompressible, which means that the volume remains constant. If νᵢⱼ=0, a stretching causes no lateral contraction. The shear modulus Gᵢⱼ indicates the material response to shearing strains. It is positive and smaller than Eᵢ.
The stiffness matrix $C_{iklm}$ of an orthotropic linear elastic material can be written as shown below:

\[
C = \begin{bmatrix}
C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\
C_{12} & C_{22} & C_{23} & 0 & 0 & 0 \\
C_{13} & C_{23} & C_{33} & 0 & 0 & 0 \\
0 & 0 & 0 & C_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & C_{55} & 0 \\
0 & 0 & 0 & 0 & 0 & C_{66}
\end{bmatrix}
\]  

(A.1)

The inverse of this matrix is a compliance matrix $S_{iklm}$:

\[
S = \begin{bmatrix}
\frac{1}{E_1} & -\frac{v_{12}}{E_2} & -\frac{v_{13}}{E_3} & 0 & 0 & 0 \\
-\frac{v_{12}}{E_2} & \frac{1}{G_{23}} & 0 & 0 & 0 & 0 \\
-\frac{v_{13}}{E_3} & 0 & \frac{1}{G_{23}} & 0 & 0 & 0 \\
0 & 0 & 0 & \frac{1}{G_{44}} & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{1}{G_{55}} & 0 \\
0 & 0 & 0 & 0 & 0 & \frac{1}{G_{66}}
\end{bmatrix}
\]  

(A.2)

where $E_i$ is the Young's modulus along axis $i$, $G_{ij}$ is the shear modulus in direction $j$ on the plane whose normal is in direction $i$, and $v_{ij}$ is the Poisson's ratio that corresponds to a contraction in direction $j$ when an extension is applied in direction $i$.

Recall that according to the generalized Hooke’s law for orthotropic medium [1], we have the following expressions:

\[
\begin{bmatrix}
\sigma_{11} \\
\sigma_{22} \\
\sigma_{33} \\
\sigma_{23} \\
\sigma_{13} \\
\sigma_{12}
\end{bmatrix} = \begin{bmatrix}
C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\
C_{12} & C_{22} & C_{23} & 0 & 0 & 0 \\
C_{13} & C_{23} & C_{33} & 0 & 0 & 0 \\
0 & 0 & 0 & C_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & C_{55} & 0 \\
0 & 0 & 0 & 0 & 0 & C_{66}
\end{bmatrix} \begin{bmatrix}
\varepsilon_{11} \\
\varepsilon_{22} \\
\varepsilon_{33} \\
\varepsilon_{23} \\
\varepsilon_{13} \\
\varepsilon_{12}
\end{bmatrix}
\]

Note that for isotropic materials:

$C_{1111}=C_{2222}=C_{3333}=C_{11}=C_{22}=C_{33}$ – compression (or elongation) deformation along each of $X$, $Y$, $Z$ axes, when e.g. stress $\sigma_{11}$ and strain $\varepsilon_{11}$ are both along this axis.

$C_{1122}=C_{1133}=C_{2233}=C_{3311}=C_{3322}=C_{12}=C_{13}=C_{23}$ – compression (or elongation) deformation along each of $X$, $Y$, $Z$ axes, when e.g. stress $\sigma_{11}$ and strain $\varepsilon_{22}$ are along different axes.

$C_{1212}=C_{1313}=C_{2323}=C_{44}=C_{55}=C_{66}$ – shear deformation in each plane $XY$, $XZ$, $YZ$ axes, when e.g. stress $\sigma_{12}$ and strain $\varepsilon_{12}$ are both in the same plane.
At the same time, for orthotropic material we have more complex expressions:

\[ C_{1111} = C_{11} = (1 - \nu_{yz} \nu_{zy})/(E_y E_z \Delta), \]
\[ C_{1122} = C_{12} = (\nu_{yx} + \nu_{xy} \nu_{yz})/(E_y E_z \Delta), \]
\[ C_{1133} = C_{13} = (\nu_{zx} + \nu_{xz} \nu_{zy})/(E_y E_z \Delta), \]
\[ C_{2222} = C_{22} = (1 - \nu_{zx} \nu_{xz})/(E_z E_x \Delta), \]
\[ C_{2233} = C_{23} = (\nu_{zy} + \nu_{zy} \nu_{zx})/(E_z E_x \Delta), \]
\[ C_{3333} = C_{33} = (\nu_{xy} + \nu_{yx} \nu_{yz})/(E_x E_y \Delta), \]
\[ C_{3311} = C_{31} = (\nu_{xz} + \nu_{xz} \nu_{xy})/(E_x E_y \Delta), \]
\[ C_{1212} = C_{44} = 2G_{yz}, \]
\[ C_{1313} = C_{55} = 2G_{zx}, \]
\[ C_{2323} = C_{66} = 2G_{xy}, \]
\[ \Delta = (1 - \nu_{xy} \nu_{yx} \nu_{yx} - \nu_{yz} \nu_{zy} - \nu_{zx} \nu_{xz} - 2 \nu_{xy} \nu_{yz} \nu_{zx})/(E_x E_y E_z). \]

Using formulae presented above we can determine the speeds of propagation of UT waves in different directions:

Along axis (1): longitudinal wave \( V_L^{(1)} = \sqrt{(C_{11}/\rho)} \),
shear wave polarized along axis (2) \( V_{S2}^{(1)} = \sqrt{(C_{66}/\rho)} \),
shear wave polarized along axis (3) \( V_{S3}^{(1)} = \sqrt{(C_{55}/\rho)} \).

Along axis (2): longitudinal wave \( V_L^{(2)} = \sqrt{(C_{22}/\rho)} \),
shear wave polarized along axis (1) \( V_{S1}^{(2)} = \sqrt{(C_{66}/\rho)} \),
shear wave polarized along axis (3) \( V_{S3}^{(2)} = \sqrt{(C_{44}/\rho)} \).

Along axis (3): longitudinal wave \( V_L^{(3)} = \sqrt{(C_{33}/\rho)} \),
shear wave polarized along axis (1) \( V_{S2}^{(3)} = \sqrt{(C_{55}/\rho)} \),
shear wave polarized along axis (2) \( V_{S3}^{(3)} = \sqrt{(C_{44}/\rho)} \).

Using known value of density \( \rho \) for ZrNb and expressions (A.4) for propagation speeds of various UT waves, we can measure all nine propagation speeds (see Table 3 in section 3.1) and then express all non-zero components of stiffness matrix of ZrNb via measured values of speeds. After that, using the obtained values of \( C_{ik} \) and formulae (A.3), we can calculate the elastic moduli \( E_i, \nu_{ij} \) and \( G_{ij} \) of ZrNb (note that number of equations in (A.3) is equal to number of unknowns.

Reference