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Criteria for the onset of structural integrity degradation due to high-temperature hydrogen attack of a carbon- manganese steel

R. J. Mostert[a,*], A. van Zyl[a], C. C. E. Pretorius[a] and V. M Mathoho[a]

Department of Materials Science and Metallurgical Engineering, University of Pretoria, Private Bag X 20, Hatfield 0028, South Africa

Abstract

Samples of a pressure vessel C-Mn steel were exposed to 46 bar pure hydrogen at 550 °C in an autoclave for various exposure periods. Some samples were instrumented with a high-temperature strain gauge to track the accelerated expansion strain in order to evaluate the extent of embrittlement. Samples of all three orientations relative to the plate rolling direction were thereafter subjected to tensile testing. The results demonstrated that severe degradation of the tensile ductility occurred after experiencing expansion strains much smaller than that anticipated earlier, especially for samples in the plate through-thickness orientation. For these samples, the critical HTHA strain, as far as through-thickness tensile ductility is concerned, could be identified as being in the order of 9 με or a strain rate of 0.4 με/ h. After approximately 28 με expansion or 0.82 με/ h, through-thickness ductility degradation approached 100 %. Two other criteria for rapid HTHA degradation were also evaluated. A critical Pw-value, derived from the McKimpson and Shewmon work for low pH_2 conditions of $P_W^{cr} = 8.15$ was determined experimentally. It was also shown that the critical ductility degradation index of Φ_R = 15 %, when applied to the through-thickness sample orientation, would serve as an early indicator for rapid degradation in the bi-axial plate loading directions. was used. Comparison of the current critical values for rapid damage with those published earlier, indicate that the current values are more realistic and accurate as fair as critical strain and P_w – values are concerned. The critical strain values published earlier were found to be non-conservative as far as through-thickness property degradation is concerned.

Keywords: HTHA; hydrogen attack; structural life assessment; materials degradation; embrittlement

* Corresponding author. Tel.: +27-12420-4551.
E-mail address: roelf.mostert@up.ac.za

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1. Introduction

Process equipment operating at high temperatures and hydrogen pressures, run the risk of being degraded by the damage mechanism of high-temperature hydrogen attack (HTHA). This insidious damage mechanism has an inherent risk of high-consequence equipment fracture, and such catastrophic failure incidents with high impact regarding cost, safety and institutional reputation have been reported from time to time (Poorhaydari, 2019). The mechanism is due to the reaction of adsorbed atomic hydrogen with carbon, resulting in methane bubble nucleation and growth, followed by bubble coalescence and fissuring, which can then lead to low-energy fracture. Mitigation of the associated risks is normally achieved by appropriate alloy selection since more stable alloyed carbides can be utilized which are known to be not susceptible for given process conditions. These interrelationships between process temperature, hydrogen partial pressure, alloy type and susceptibility are defined by so-called "Nelson Curves" which have first been published by the American Petroleum Institute (API) in 1949 (Nelson, 1949). The curves are based on industry experience and, especially in the case of lower alloyed steels, have been adjusted downwards to lower operating conditions from time to time, due to new cases of damage being reported as time progresses. Consequently, many process units, especially those constructed some years ago from C and C – 0.5 Mo alloys, are currently operating in process conditions which had earlier been regarded as low-risk, but where current knowledge have identified the units to be at risk. In addition, the growth of the hydrogen economy will lead to significant growth in the number of process units operating at elevated hydrogen pressures and temperatures, necessitating improved knowledge and mitigation of HTHA. The current study therefore has the objective of quantifying criteria that can be used to identify the onset of HTHA damage in structural carbon steels.

2. Measures of HTHA degradation and associated criteria

Over time, a number of criteria have been identified to indicate the onset of HTHA damage:

2.1. HTHA strain and microstructures

Due to the initiation, growth and coalescence of methane bubbles, the process of HTHA degradation is inherently associated with expansion over time. Early studies of HTHA kinetics used dilatometry to measure the strain that develops due to the damage (Sundararajan and Shewmon, 1980), and, more recently, Mostert et al (2022) showed that advanced encapsulated high-temperature strain gauges can be used to sensitively track HTHA damage both in the laboratory and in structures. These encapsulated strain gauges by Kyowa (2022) are spot welded onto the surface to be monitored and the resulting strain-life curves have been shown to be sigmoidal in nature. The process of damage and strain evolution over time can therefore be mathematically described if a number of empirical constants are known for the steel and process conditions. This development holds promise for the mitigation of risk in structures that have been identified as being potentially susceptible to HTHA. In previous work, Mostert et al (2022) hypothesized that the extent of HTHA damage evolution can be tracked by analyzing the derivatives of strain-life curves, even if the full set of constants are not known.

The classic HTHA studies, using dilatometrical and other laboratory equipment, distinguished between the early period of slow HTHA damage, the "incubation period", followed by region of rapid attack where the strain rate "accelerated sharply". McKimpson and Shewmon (1981) found that this border between low strain rates and the region of "rapid attack", was at a strain value in the order of 1000 micro-strain ($\mu\varepsilon$), for moderate pH_2 values (4.4 MPa) and 400 to 500 $\mu\varepsilon$ for higher pressures and lower temperatures.

Damage evolution based on microstructural degradation and its association strain evolution can be expected to be closely associated with the degradation of mechanical properties. Early research theorized that the end of the incubation period will be reached when bubbles located on grain boundaries grow through diffusion of Fe atoms from the bubble face to grain boundaries, up to the point where a continuous bubble has formed on a grain boundary face. Shewmon (1985) linked the end of the incubation period and the start of the "rapid attack" region of the HTHA strain curve, with the bubbles "linking up to form a single bubble over a grain boundary segment". The correspondence between the strain-time inflection point at relatively low strains and mechanical property degradation has however not been fully explored. Munsterman (2010) has for instance shown that the full HTHA damage development for carbon steels are associated with levels of strain in the order of 21 000 με. An important question is therefore related to the progress of mechanical property degradation as prior to and during the rapid attack phase of HTHA. As an example, it is important to determine to what extent mechanical property degradation is associated with the 400 – 1000 με threshold and how it progresses thereafter. Knowledge of this behaviour will be very beneficial in tracking mechanical property degradation and remaining life using encapsulated high-temperature strain gauges.

The concept of a threshold for rapid HTHA attack has been utilized by industry bodies in standards and recommended practices from early times. API 941, 1977 edition, for instance, published curves for HTHA damage initiation as a function of hydrogen partial pressure and temperature. Curves are presented therein for "incubation times" ranging from 100 h to 10 000 hours, for carbon steels. The meaning of these curves regarding the extent of mechanical property degradation and the onset of rapid embrittlement is however unclear.

2.2. Ductility degradation index

Classic HTHA studies, such as that of Weiner (1961) demonstrated that plots of ductility degradation vs exposure time produced curves with three distinct regions, similar to that observed with strain measurements. An initial incubation period was observed, where little to no loss of ductility was observed, followed by a period of rapid attack, where embrittlement proceeded rapidly. The third stage was that of damage saturation, which showed a reduced rate of embrittlement. These studies however did not correlate the transition time to rapid embrittlement to the corresponding times on the strain-time curves.

Since the major structural integrity risk associated with HTHA is that of low-energy brittle fracture, it is sensible to measure the extent of degradation as a function of mechanical properties that reflect the propensity for such failure. As reported by Liu (2001) the JPVRC has since 1987 defined and utilized four parameters to quantify the extent of HTHA damage on mechanical properties of C -0.5 Mo steels. The ductility degradation index (Φ_R), for instance, was defined as:

$$\Phi_R(\%) = \frac{R_0 - R}{R_0} \tag{1}$$

where R_0 and R refer to the reduction of area before and after HTHA exposure, respectively. The other index used was the toughness degradation index, Φ_E with a similar definition. More recently, Hattori (1997) stated that the JPVRC is using a 15 % Φ value, either due to Φ_R or Φ_E, as a criterion for confirmation of hydrogen damage, alongside with microstructural criteria (see 2.4). The other two paraments, according to Liu (2001) are the P_w and P_v parameters, discussed in Section 2.3 below.

2.3. Hydrogen attack parametric models

The classic study by McKimpson and Shewmon (1981), using dilatometry, showed that the kinetics of early HTHA damage follows an Arrhenius relationship:

$$\frac{d\varepsilon}{dt} = A\left(P_{H_2}\right)^{\boldsymbol{\alpha}} \exp\left(-\frac{Q}{RT}\right) \tag{2}$$

For ASTM A516 pressure vessels steels at relatively low H_2 pressures and temperatures, **with T in Kelvin and t in hours** equation (2 becomes equation (3:

$$\frac{d\varepsilon}{dt} = 51.6\left(P_{H_2}\right)^{\mathbf{1.9}} \exp\left(-\frac{115}{RT}\right) \tag{3}$$

The P_w and P_v hydrogen attack parameters have their bases in Arrhenius relationships such as equations 3 and 4 and reflect the level of HTHA attack following exposure at a H_2 pressure expressed in MPa, for a time in hours, and at a temperature in Kelvin. Several versions of these parameters have been developed for specific cases, and a very applicable parameter has been developed, based on equation (3, by Nomura and Sakai (2008).

$$P_w = -1.9 ln P_{H_2} - lnt + \left(\frac{11500}{8.3145T}\right) \tag{4}$$

Using a "critical strain" of 400 με for the onset of rapid attack and using equation 4, a critical value of P_W was accordingly proposed by Nomura and Sakai (2008) as being, $P_W^{cr} = 11.768$. The correlation of such hydrogen attack parameters with the progression of mechanical property degradation for steels is of obvious importance and have also been used with success on establishing P_W^{cr} values for Φ_R degradation of C -0.5 Mo steels, as reported by Liu (2001) . Considerable variability in such critical values of P_W is however found, depending on the source data used. If, for instance, the appropriate hydrogen pressure data points from the carbon steel "incubation time" curves according to API 941 2006, referred to in Section 2.1 above, are applied to equation 4, a P_W^{cr} value of 13.9 is obtained. This value predicts the onset of HTHA damage at much earlier stages than that of value based on the work of McSimpson and Shewmon (1981), with a value of $P_W^{cr} = 11.768$. It should be noted that the basis for both these P_W^{cr} -values are based in steel manufactured prior to 1980, reflecting older steelmaking practice. In the current work, critical values will be determined for an ASTM 516 steel produced using modern steelmaking practices.

2.4. Microstructural criteria and influences

Pretorius et al (2022) has shown a strong directionality effect of the swelling strains in C-0.5Mo steels, as measured by high-temperature encapsulated strain gauges. The largest strains were associated with strain orientations at right angles to the rolling direction, in the case of hot-rolled plate. This effect was observed to be due to the directionality of damage, in the case of pearlite or carbide bands being present in the microstructures. Accordingly, grain boundaries which were in-plane with the rolling direction developed more damage that others, and the strains perpendicular to these boundaries (and the rolling direction), were accordingly greater than in in the other directions. It is believed that this observation is pertinent to the development of mechanical degradation and its kinetics in pressure vessel C-steels, an aspect that has not received much research attention to date. Early classical studies of the development of mechanical degradation, such as that by Weiner (1960), have often not reported sample orientation, which contributes to the difficulty of correlating reported mechanical property and microstructural degradation rates, via strain measurements.

According to Poorhaydari (2021) microstructural degradation damage, in the form of the observation of bubbles or fissures on grain boundaries at a magnification of 2000 x, is also used by the JPVRC to identify the onset of damage, together with the 15 % Φ degradation criterion mentioned in 2.2 above. It is unclear if it is believed that the microstructural and Φ- degradation criteria are believed to be correlated and equivalent.

3. Aims of the study

Due to the above gaps in the current knowledge regarding HTHA degradation development of carbon steels, it was decided to evaluate the development of microstructural degradation, via strain measurements, and mechanical property degradation, via tensile testing, on an ASTM A 516 Grade 70 pressure vessel steel, manufactured according to current practices. The mechanical property degradation would be evaluation in all three directions relative to the rolling direction. The results will be interpreted using the P_w – parameter of equation 4.

4. Experimental

A 40 mm thick hot rolled carbon – manganese steel plate with composition shown in Table 1, was acquired.

Table 1. Chemical composition of 40 mm plate

	C	Mn	Si	P	S	Al
ASTM A 516 Gr 70 specification	0.28 max	0.79 – 1.3	0.3 max	0.035 max	0.035 max	-
Plate analysis	0.16	1.41	0.30	0.016	0.005	0.032

Tensile samples were machined with the gauge lengths oriented in the longitudinal (L) transverse (T) and through-thickness (Z) directions, with respect to the rolling direction. Samples of service-exposed steel (nominal conditions are 350 °C and 25 bar H_2) of the same grade were subjected to SEM microscopy to evaluate the likely location and orientation of damage, to aid with the experimental planning. It was found that a banded microstructure was prevalent, and that the grain boundaries associated with the bands were preferentially attacked (Figure 1). It was therefore expected that mechanical property degradation would be most pronounced in the Z- direction, and most of the samples were therefore prepared in that orientation (15 samples). The L and T samples (8) were machined according to ASTM E8, gauge dimensions 36 mm x 9 mm, and the Z -samples were machined to ASTM A 770 Type D.

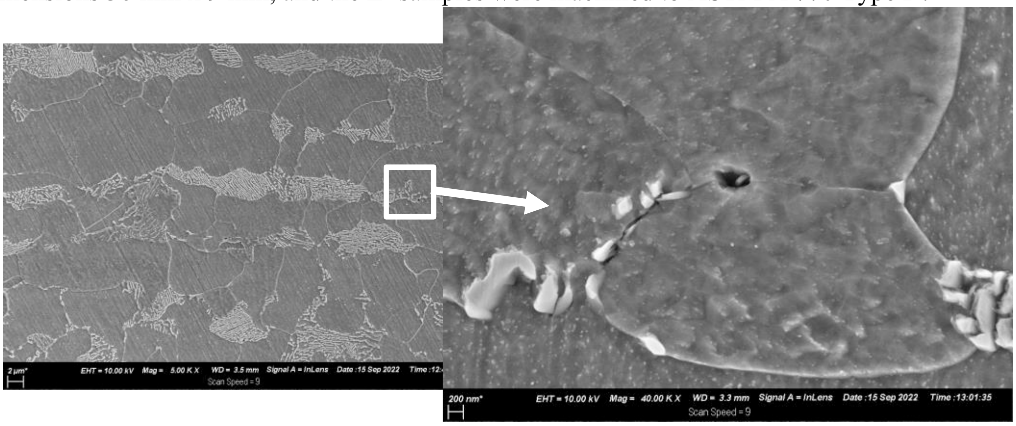

Fig. 1. SEM images of service exposed ASTM A 516 Gr 70 plate (a) 500 X ; (b) 4000 X nominal magnification

The swelling strain was monitored in an experimental autoclave set-up, with an encapsulated high-temperature strain gauge attached to a polished through-thickness sample, 32 mm x 10 mm x 3mm, taken from the plate. Pretorius et al (2022) described the experimental configuration in detail elsewhere. Autoclave exposure of the tensile and strain - life samples were performed at 550 °C and 46 bar H_2 pressure.

5. Results

The HTHA strain – time curves are presented in Figure 2. Figure 2 (a) compares the experimental results with equation 5 developed earlier by Mostert et al (2022) and which describes the HTHA degradation behavior, showing good correlation. The specific equation for this steel, conditions, and sample orientation is reflected in equation 6:

$$y = A_2 + \frac{A_1 - A_2}{1 + \exp\left(\frac{t - X_0}{dx}\right)} \tag{5}$$

Or

$$\varepsilon = 6347 - \frac{6347}{1 + \exp\left(\frac{t - 525.4}{31.8}\right)} \tag{6}$$

with ε in με and t in hours.

Accordingly, HTHA microstructural damage and its associated strain is seen to increase significantly from ~ 300 hours onwards, with a peak in strain and damage development rate observed at 525 hours (figure 2 b). During the early stages of the damage development, some strain development was observed, although at a lower level (see Figure 5).

The ductility degradation index vs time plots are presented as Figure 3. For the determination of reduction of area, each sample was subjected to at least ten stereo microscopic measurements, before and after exposure. For the 15 samples tested for the Φ_{Rz} -curve in Figure 3, Φ_{Rz} values were capped at 0 if negative values, probably due to surface decarburisation, were found. For the L- and T- samples, little difference was observed in 8 Φ_R -values established and one Φ_{RLT} - curve was therefore developed**.** The L and T tensile samples required longer times for degradation compared to that of the Z-samples and, consequently, more samples of these orientations will be tested in future to confirm the full curve. The same shape of the Φ_{Rz} -curve was fitted to the L and T sample data points currently available, which appears in keeping with the Φ_R results published by others such as Weiner (1960) in order to evaluate the L and T trends with the available data.

The Φ_R results demonstrate that the onset of degradation occurs at relatively short times, associated with very low swelling strain and strain rate values. Furthermore, once initiated, the degradation progress is relatively rapid. The fact that the Φ_{Rz} -curve precedes the "rapid attack" region of the strain-life curve is obviously an important finding.

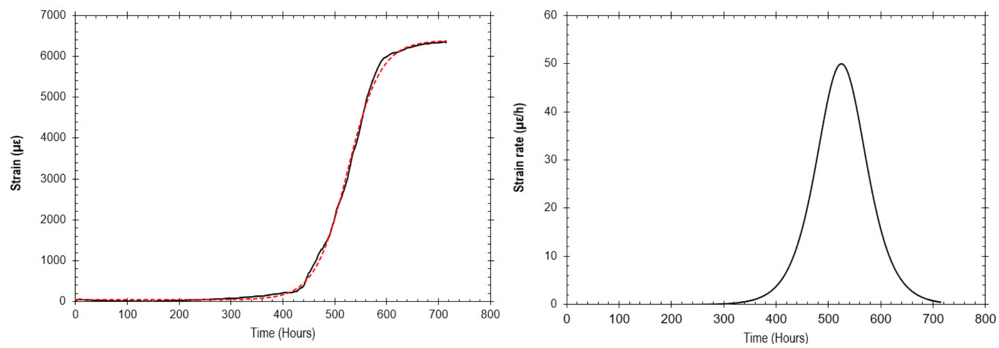

Fig. 2. HTHA strain – time curves, left, original curve (solid line) and mathematical equation fitted (dashed curve); right, strain rate – time curve.

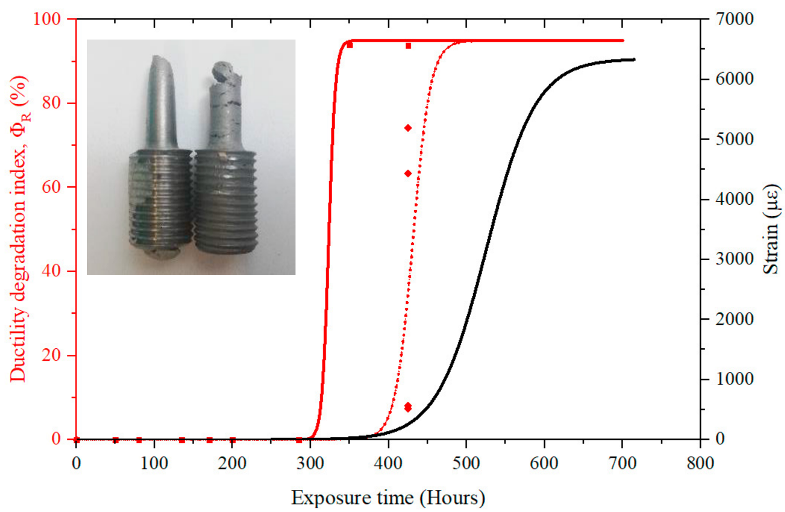

Fig. 3. Ductility degradation index versus exposure time curves, with HTHA strain – time curve included for reference. Curves from left to right, Φ_R of Z- orientation samples, Φ_R of L, T - orientation samples , strain-time of Z-orientation sample. The photograph shows two through-thickness (Z) samples after tensile testing, one unexposed (left), one exposed for 350 hours (right).

6. Critical degradation values

6.1. Ductility degradation index

According to Fig. 3, the critical value of the ductility degradation index in use by the JPVRC, $\Phi_R = 15$ %, is clearly a value that confirms that the steel ductility is in the process of being degraded through HTHA (with $R_{A0} = 75.4$ %, a 15 % degradation implies a drop to $R_A = 64.1$ %). At this level of degradation, the mechanical properties are not seriously degraded but with a small increase of exposure time, degradation became very severe (see photograph inserted in Fig. 3 for the extent of degradation observed after 350 h of exposure). The $\Phi_R = 15$ % criterion therefore appears to be insufficient for purposes of "early warning" with a view to mitigation or replacement of the affected equipment. The damage progression curve is quite steep and the time difference between $\Phi_R = 15$ % and $\Phi_R = 50$ %, where structural integrity would be seriously threatened, if adapted to typical operational conditions such as those mentioned in Section 3 above, and using the Pw-parameter of equation 4, amounts to only 6500 hours or 0.74 years. Such a period would typically be insufficient to prepare for replacement plans and parts in a continuous process environments.

In cases where the through-thickness loading is low and where Z- direction ductility degradation has little impact on structural integrity, such a criterion would however provide sufficient warning for degradation in the other (L and T) load-bearing directions. The time difference between $\Phi_{RZ} = 15$ % and $\Phi_{RLT} = 15$ %, adapted to the process conditions of 350 °C and P_{H2} of 25 bar, amounts to a period of 7.7 years, which is obviously adequate for replacement planning.

6.2. Hydrogen attack parameters, P_w

In Fig. 4 a, the HTHA degradation response studied here is presented as a function of the low- medium pressure Pw parameter of equation 4. Accordingly, a critical value for $\Phi_{Rz} = 15$ % has been identified as resulting in a critical P_w value of $P_{WZ}^{cr} = 8.15$, which can be regarded as being applicable to modern carbon- manganese pressure vessel steels in the through-thickness orientation. This value implies a HTHA life of 25.3 years for the 350 °C and 25 bar P_{H2} process conditions. $P_{WL,T}^{cr}$ will be slightly smaller, but it is proposed that the $P_{WZ}^{cr} = 8.15$ value be used to enhance conservatism.

Comparison of the $P_W^{cr} = 8.15$ determined here for carbon- manganese pressure vessel steels to that originating from other data sources, indicates a large extent of variability. In the classic work of Weiner (1960), for example, a steel similar to the currently investigated steel was subjected to temperatures and hydrogen pressures similar to the current values. Plots of degradation against time were developed at each temperature. These plots allow the determination of P_W^{cr} using equation 4, and the average value in the temperature range 427 °C to 593 °C at a pH_2 of 48.26 bar, yields a Weiner $P_W^{cr} = 11.1$ (based on $\Phi_R = 15$ %), which is similar to the $P_W^{cr} = 11.768$ based on a 400 με value as propped by Nomura and Sakai (2008). Adapted to the operating conditions of 350 °C and 25 bar P_{H2}, this value (11.1) implies a significantly reduced HTHA life of 11 600 hours (1.32 year). Similarly, the adapted API 941 curves for "incubation times" yielding a P_W^{cr} of 13.9, implies a process service life of only 700 hours for carbon steels at 350 °C and 25 bar P_{H2}. Clearly more research is required concerning the factors that could influence the observed variability of critical P_w – values.

6.3. HTHA strain

In the early stages of the HTHA strain-time curve, an incubation time of ~ 200 hours is observed, when the strain developed is consistently less than 0.25 micro-strain, with an exponential increase observed thereafter (Fig. 4b). Accordingly, the critical strain values corresponding to the critical ductility degradation of $\Phi_{RZ} = 15$ % in the through-thickness orientation, is 9 micro-strain and a strain rate of 0.24 micro-strain per hour. The experimentally determined critical HTHA strain value is therefore considerably lower than the range of 400 – 1000 micro-strain considered earlier as critical thresholds by Nomura and Sakai (2008) and McSimpson and Shewmon (1981). For the current case, the point of transition from "slow damage" to "rapid attack" of the through-thickness strain-time curve corresponds to a strain value of ~ 500 microstrain, clearly indicating the merit of the values quoted in the classical works. It is however possible that the critical strain value of 9 microstrain for through-thickness samples, is much more severe than that for sample in the other orientations.

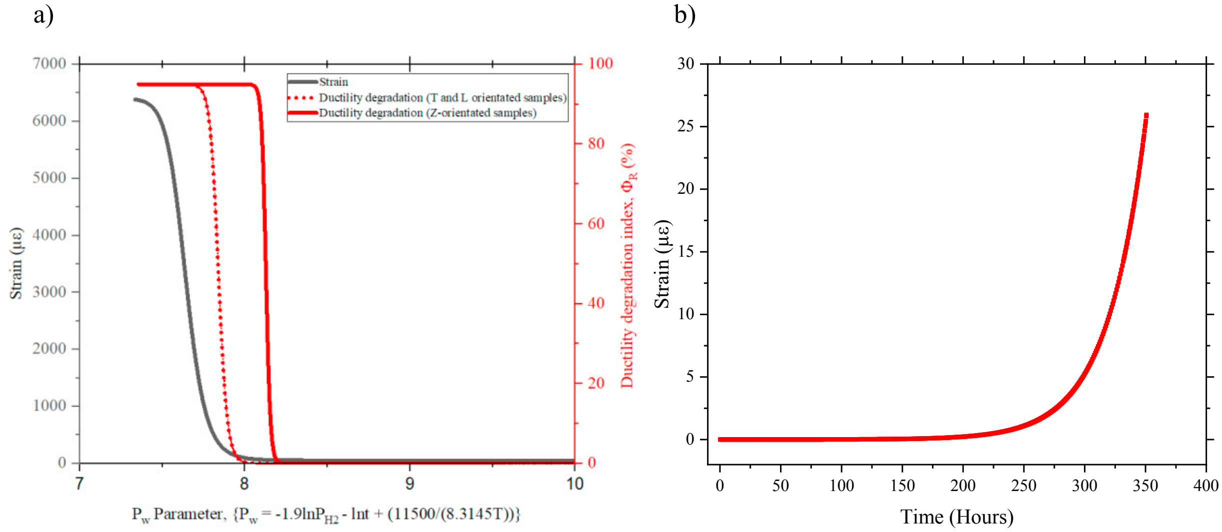

Fig. 4 (a) Degradation Index and HTHA strain – time curves as a function of the Pw parameter ; (b) Early stages of the HTHA strain curve

7. Discussion and Conclusions

Three criteria for critical HTHA degradation have been established with different applications as far as HTHA monitoring and mitigation are concerned:

- The critical Φ_{RZ} value of 15 % has been shown to be a good early indicator of mechanical property degradation in the longitudinal and transverse orientations. Regular removal of through-thickness samples from at-risk equipment can be used to track the degradation over time in order to arrange mitigation measures prior to experiencing extensive embrittlement.
- The established critical P_w- value of $P_W^{cr} = 8.15$ can be used to evaluate the criticality of process conditions and elapsed time for carbon steels of recent origin. It should be used with caution with carbon steels of older heritage.
- The critical strain and strain rate values of 9 micro-strain and 0.21 micro-strain per hour, respectively, can be used for continuous monitoring of components in the through-thickness orientation, using high-temperature encapsulated strain gauges. In addition, samples extracted from process equipment and subjected to laboratory testing, can be evaluated for critical damage by comparing the laboratory strain rate values to the stated critical value.

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